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By
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2.0 CONTROL TECHNOLOGY AND COAL PREPARATION RESEARCH

2.1 Flue Gas Cleanup

FLUE GAS CLEANUP

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

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FLUE GAS CLEANUP

1.0 INTRODUCTION

From April 1983 through March 1988, the focus of the Cooperative Agreement SO_x/NO_x Control project was investigation of dry sorbent injection for SO_x control and methods of enhancing SO_x sorbent reactivity/utilization. The primary emphasis was furnace injection of calcium-based sorbents with some experiments evaluating back-end humidification (1,2). In April 1988, the emphasis of the project was changed to advanced NO_x control with application to new and existing utility systems, as well as control of NO_x emissions from industrial-scale combustors. Specific activities for the period April 1988 through June 1989 focused on the bench-scale evaluation of a catalyst-coated woven fabric filter for simultaneous NO_x and particulate control (3). In June 1989, the project name was changed from SO_x/NO_x Control to Flue Gas Cleanup, and the scope of project activities was expanded to include tasks supporting bench-scale work in the fine-particulate control area. Work in the fine-particulate control area was included as a separate project within the Cooperative Agreement from April 1983 through March 1988 and was also funded as a result of a competitive DOE award during the period May 1988 through December 1989.

In March 1990, the Energy and Environmental Research Center (EERC) was notified that a proposal, in response to RFP DE-RP22-89PC89801 entitled "Development of Advanced NO_x Control Concepts for Coal-Fired Utility Boilers," was selected for funding. Therefore, catalytic fabric filter development activities have been deleted from the Cooperative Agreement Flue Gas Cleanup project.

At the request of Department of Energy-Pittsburgh Energy Technology Center (DOE-PETC), a task was added this year (July 1, 1991 through June 30, 1992) to assess the effect of coal combustion on visibility impairment in the atmosphere. Therefore, the Flue Gas Cleanup project is currently focusing on two areas: 1) bench-scale efforts to further investigate the relationships between fine-particle emissions from fabric filters and the cohesive properties of fly ash, and 2) investigation of the impact of coal combustion on atmospheric visibility.

This report documents the work for the Flue Gas Cleanup project for the period January 1 through June 30, 1992.

2.0 BACKGROUND

Present New Source Performance Standards for utility coal-fired boilers limit particulate emissions to 0.03 lb/million Btu and require 20% or lower opacity. The control device removal efficiency required to meet this standard varies from about 99% to 99.9%, depending on the heating value and ash content of the coal. Electrostatic precipitators or fabric filters are the technologies that have most often been employed to meet the current standard. Although the best proven control technology for fine-particulate matter appears to be fabric filtration if it is properly designed, both of these technologies have been successful, in most cases, in meeting the current standard. However, the removal efficiency of both electrostatic precipitators

and baghouses is significantly reduced for fine particles less than 2 μm . Emissions of fine particles are of concern because these particles are likely to be deposited in the lower respiratory system through normal breathing. The problem is further compounded because hazardous trace elements such as selenium and arsenic are known to be concentrated on such fine particles. Control device removal efficiency is lowest for respirable particles, so a situation exists where the most hazardous particles from coal combustion are collected with the lowest removal efficiency. In addition to causing adverse health effects, fine-particle emissions have an impact on atmospheric visibility. Particles which are the most efficient at scattering light (0.1-2 μm) do not readily settle out of the atmosphere and are subject to long-range transport. When present in sufficient concentrations, these fine particles will cause serious visibility impairment. Therefore, the emission of fine particles is an issue because of potential adverse health effects and visibility impairment in the atmosphere.

Previous results at the EERC show that fine-respirable-particulate emissions can be reduced by up to 4 orders of magnitude by injecting small amounts of ammonia and SO_3 upstream of a baghouse (4-15). This corresponds to an increase in collection efficiency, for some difficult-to-collect ashes, from 90% to 99.999%. Emissions in some tests are less than ambient particulate levels in the atmosphere. Along with reduced particulate emissions, baghouse pressure drop is also reduced, making the process more economical. With some coals, pressure drop was reduced by 75%. Conditioning would add about 9% to the cost of operating a conventional reverse-gas baghouse, but this cost could be more than recovered if pressure drop and/or size of the baghouse is reduced.

The conditioning agents make the ash particles more cohesive which reduces the seepage of dust through the fabric and facilitates the bridging of pinholes, preventing direct particle penetration. At the same time, a more porous dust cake is formed, which results in reduced baghouse pressure drop. A review of penetration mechanisms shows that there is a theoretical basis for lower emissions with increased bulk cohesive strength. Pressure drop reduction as a result of conditioning is attributed to an increase in dust cake porosity as theoretical and empirical models predict. To further develop this technology the cohesive characteristics of fly ash must be quantified and related to fabric filter performance. There is a need to test existing methods and select or develop reliable methods to measure cohesive properties of fly ash. Further, the measured cohesive properties should be correlated with other ash properties to understand which ash properties control cohesive strength and to help understand how ash properties affect fine-particle emissions from fabric filters.

In 1977, Congress added Section 169A to the Clean Air Act (CAA) which established as a national goal "the prevention of any future, and the remedying of any existing, impairment of visibility in mandatory Class I Federal areas which impairment results from man-made air pollution." The Environmental Protection Agency (EPA) defines "visibility impairment" as "any humanly perceptible change in visibility (visible range, contrast, coloration) from that which would have existed under natural conditions." The EPA has identified two types of air pollution that impair or reduce visibility. The first is single-source impairment defined by the EPA as smoke, dust, colored gas plumes, or layered haze emitted from stacks that obscure the sky or horizon, and are relatable in a single source or a small group of sources.

The second type is regional haze which is widespread, regionally homogeneous haze from a multitude of sources, and impairs visibility in every direction over a large area. The EPA has used a phased approach to implement the visibility program. Phase I of the program requires control of impairment that can be traced to a single existing stationary facility or small group of existing stationary facilities. Section 169B was added to the CAA in 1990 to determine the need for expansion of the visibility protection program. It provides funding for continued research on visibility in Class I federal areas including: 1) expansion of current visibility impairment monitoring, 2) assessments of current sources of visibility impairment using regional air quality models, and 3) studies on atmospheric chemistry and the physics of visibility. Section 169B also calls for the creation of Visibility Transport Regions consisting of one or more states which, because of interstate pollution, contribute significantly to visibility impairment in Class I areas. After the creation of Visibility Transport Regions, Visibility Transport Commissions (VTCs) (whose members include the Governors of the affected states) will be formed to address the establishment of clean air corridors, restrictions on new construction, and the development of long-range strategies for remedying regional haze.

Visibility has been the focus of a significant amount of research for over a decade. However, attempts to accurately identify the contributions of various sources to visibility impairment have been hampered by the limitations of air quality models and the lack of understanding of the complex physical and chemical processes that govern the formation of secondary aerosols in the atmosphere.

3.0 GOALS AND OBJECTIVES

The general objective of the DOE Flue Gas Cleanup Program, under the direction of the PETC, is to promote the widespread use of coal. This is to be accomplished by providing the technology necessary for utilization of coal in an environmentally and economically acceptable manner. The program addresses the reduction of acid rain precursor emissions as well as development of technologies with the potential to meet more stringent emissions control requirements for SO_2 , NO_x , and particulate matter.

For this current project year, only the fine-particulate control area of the DOE Flue Gas Cleanup Program is addressed. Specific activities involve the development of methods to measure the cohesive strength and reentrainment potential of fly ashes relative to fine-particle emissions from fabric filters and an assessment of the impact of coal combustion on atmospheric visibility. The general objective of the fine-particulate control effort is to develop methods to help characterize, control, and model fine-particulate emissions from a fabric filter. Characterization efforts include the development of methods to measure the cohesive strength and reentrainment potential of fly ashes. Control and modeling efforts involve relating these parameters to the level of fine-particle emissions from fabric filters. Specific goals this year include the following:

1. Correlate measured cohesive strength with other ash properties such as particle size, particle shape, surface area, porosity, and ash chemistry.

2. Measure the reentrainment potential of ash from the surface of a fly ash filter cake or bulk fly ash and relate it to the measured cohesive strength.
3. Perform a literature review to determine the status of the visibility issue as it relates to coal combustion. Based on the information collected, prepare a multiyear work plan for the visibility activities within the Flue Gas Cleanup project.
4. Evaluate the potential for applying new particle measurement methods to atmospheric aerosols, relating the results to direct visibility measurements.

4.0 ACCOMPLISHMENTS

4.1 Fine-Particulate Control

4.1.1 Review of Previous Cohesive Measurements and Reentrainment Experiments

The bench-scale efforts this year (July 1, 1991 through June 30, 1992) were a continuation of the Fine-Particulate Control work completed last year (July 1, 1990 through June 30, 1991). Recent results were reported in the last two semiannual reports (15,16). The primary focus of the work has been to develop methods to measure the cohesive properties of fly ash and relate these properties to filtration behavior. This information should lead to a better understanding of how fly ash properties affect fine-particle emissions from fabric filters and how conditioning the fly ash improves fabric filter performance. It is expected that superior fine-particulate control can be achieved at a reduced cost compared to existing technologies, either by employing flue gas conditioning or by other design optimization methods.

Quantification of the cohesive character of fly ash for modeling fabric filter performance is analogous to the measurement of fly ash resistivity to model electrostatic precipitator (ESP) performance. Resistivity measurement provides a basis to design ESPs for a target level of collection efficiency based on a property of the dust. An equivalent measurement of the cohesive character of fly ash could provide a basis for design of fabric filters in terms of fabric selection and air-to-cloth ratio to achieve a target collection efficiency and pressure drop for a given dust. The availability of such a measurement would facilitate optimization of fabric filters to provide the highest fine-particle collection efficiency at the lowest cost. However, there is presently no consensus as to what characteristics of the fly ash should be measured or is there an accepted protocol for such measurements as tensile strength and porosity. Data suggest that both tensile strength and porosity measurements provide critical information that can be used to predict collection efficiency and pressure drop, but both approaches need further evaluation and development.

During the last two years, initial measurements were conducted with a Cohetester and a Powder Characteristics Tester. These two instruments directly measure the tensile strength and porosity of fine powders, respectively. A description of these instruments, along with the test procedures, was given in the July 1989-June 1990 annual report (14).

One of the effects of conditioning is an increase in fly ash tensile strength at constant porosity or an increase in porosity at constant tensile strength. When tensile strength was plotted as a function of porosity, the primary effect of conditioning was a shift in the curve upward (higher tensile strength) and to the right (higher porosity). Initial results also showed that the tensile strength measurements may be affected by the ambient relative humidity. Subsequent tensile strength measurements were conducted to evaluate the effect of relative humidity by exposing the samples to carefully controlled humidity conditions. Results showed that the tensile strength of baseline fly ashes were not as sensitive to relative humidity, as were the conditioned fly ashes. This indicates that there is an interaction between conditioning and relative humidity. From the measurements conducted to date, it appears that tensile strength is an excellent method to quantify the cohesive character of fly ash, and that tensile strength correlates with filtration behavior such as pore-bridging ability. However, measurement of fly ash tensile strength is still under development and is not an accepted or standard method.

Porosity and tensile strength are measures of the cohesive character of a dust, but, by themselves, do not provide any predictive indication of filtration behavior unless they can be directly correlated with filtration performance data. Previous data indicated that differences in collection efficiency in a fabric filter with different dusts could be linked to the pore-bridging ability and reentrainment potential of the dust. The fabric filter data also showed that differences in pressure drop with different dusts are tied to the specific dust cake resistance coefficient, K_2 , of the dusts. Therefore, if pore-bridging ability, reentrainment potential, and K_2 can be measured directly in the laboratory, and, if these measurements correlate with the tensile strength and porosity measurements, there is a basis for prediction of fabric filter performance from cohesive characteristics.

To better understand filtration performance, work was conducted to look at the reentrainment properties and the pore-bridging behavior of fly ash. Measurement of pore bridging and the reentrainment of conditioned and baseline fly ash was conducted as a function of pore size and face velocity. Pore-bridging and reentrainment tests showed that conditioned ash is more effective at bridging pores over the entire velocity range tested (15). An explanation is that the particle-to-particle binding forces must be greater with conditioning. However, pore-bridging ability apparently cannot be predicted on the basis of tensile strength alone because superior bridging was also achieved at lower tensile strengths. The exact physical parameters that predict pore-bridging ability, based on last year's experiments were not clear. While significant new data were added to help predict filter performance on the basis of dust properties, more work was needed. Therefore, further work was conducted this project year by adding the variables of particle size and relative humidity to pore-bridging and reentrainment tests.

4.1.2 Pore-Bridging and Reentrainment Tests

Initial tests were conducted with a reentrainment cell in which an ash layer was placed manually on a horizontal screen without air flow (14). Air was introduced downward through the layer, and particulate emissions monitored as the face velocity of air through the ash layer was slowly increased. Results showed that the velocity at which significant reentrainment occurred

depended on pore size; whether conditioned or baseline fly ash was used; and, to a lesser extent, on the level of packing of the ash layer. However, one drawback to this approach is that the ash layer was not formed from dust cake buildup during a filtration process and may not have been indicative of dust cake structure that occurs in fabric filtration. Therefore, last year, pore-bridging and reentrainment tests were conducted under actual filtration conditions. The experimental system consisted of a filter holder containing a 0.42-ft² filter sample and a dry-powder disperser to introduce the fly ash into a carrier gas upstream of the filter. The system was originally designed so that the filter could be operated at 300°F and ammonia and SO₂ could be injected upstream of the filter. Tests last year, however, were conducted at ambient temperature and without conditioning agents, although modifications were made so that relative humidity could be precisely controlled.

Pore-bridging experiments were conducted to investigate the effect of particle size and relative humidity on the pore-bridging ability of baseline and conditioned Monticello fly ash. The carrier gas was dry compressed air, with part of the carrier gas diverted through a controlled temperature water bath prior to the dry-powder disperser and filter holder. A humidity sensor was placed in the filter holder to continuously monitor the relative humidity of the air passing through the filter. By changing the fraction of gas that passed through the water bath and the water temperature, the relative humidity at the filter could easily be controlled. At the start of each test, the airflow rate was set, and background particulate levels of the clean carrier gas were measured. As expected, background particulate levels were very low and not a source of interference. Dust was then fed for a period of 35 minutes, while particulate emissions and pressure drop were recorded as a function of time. Respirable-mass-particulate emissions were measured with an aerodynamic particle sizer (APS), and submicron particles were measured with a condensation nucleus counter (CNC). Inspection of both the clean and dirty sides of the screens through sight ports gave visual proof of complete pore bridging or the formation of pinholes. A constant volumetric dust feed rate was used for all of the tests, based on a feeder piston speed of 100 mm/hr, which corresponds to about 65 grams of baseline dust and 47 grams of the conditioned dust. The weight of dust remaining on the filter at the end of each test was determined allowing calculation of K₂ values in cases where a sufficient dust cake remained intact on the filter and where pinholes were not present in significant quantities.

Pore-bridging was evaluated as a function of particle size, pore size, gas velocity and relative humidity. The particle-size effect was evaluated in the current project year by conducting additional pore-bridging tests at 15% and 50% relative humidity with the size-fractionated (4.5 μm) baseline and conditioned Monticello fly ashes. Gas velocity ranged from 1 to 8 ft/min and pore size ranged from 20 to 300 μm. Only enough tests were conducted to establish the maximum velocity at which complete bridging occurred for a given pore size rather than to complete a full matrix with these variables. For example, if results showed that complete bridging occurred with a 150-μm screen, there would be no reason to test smaller screen sizes at the same velocity. Similarly, if bridging did not occur for a given velocity with a 150-μm screen, there would be no reason to conduct a test at the same velocity with the larger 300-μm screen.

The effect of conditioning and relative humidity on the pore-bridging ability of the dusts from the screen tests is shown in Figure 1. No

improvement in pore-bridging ability was seen with the increase in relative humidity for the baseline ash. However, as Figure 1 shows, an increase in relative humidity had a dramatic effect on pore-bridging ability of the conditioned Monticello fly ash. Looking at the 150- μm screen data in Figure 1 reveals that the greatest shift in the bridging velocity vs. pore size curve was between the conditioned ash at 15% and 50% relative humidity, which is consistent with previous tensile strength data (15,16). From these observations, a good predictor of pore-bridging ability appears to be tensile strength. The maximum bridging velocity, as a function of tensile strength for the 150- μm screen, is shown in Figure 2. In Figure 2, the curve on the left was obtained from the tensile strength vs. porosity curves (extrapolating where necessary) using the dust cake porosity, which was inferred from K_2 measurements. The curve on the right was obtained using the tensile strength at the maximum compaction pressure (lowest porosity). Although the curve on the left would appear to be more valid, uncertainty is introduced because extrapolation is required to obtain the tensile strength for some cake porosities. Therefore, it may be preferable to predict pore bridging from the tensile strength data at maximum compaction pressure since it is known with

Figure 1. Effect of pore size on maximum pore-bridging velocity for screen tests with baseline and conditioned Monticello fly ash.

Figure 2. Maximum pore-bridging velocity for the 150- μm screen as a function of tensile strength.

greater certainty. Again, much more data are needed to further evaluate and refine this correlation. Plans are to continue the development of this correlation.

Figure 3 presents the effects of conditioning, particle size, and relative humidity on K_2 for the screen tests. Results show that the smaller 4.5- μm dusts had higher K_2 values, as expected. Pressure drop models, such as Carman-Kozeny, which exhibit an inverse square relationship between K_2 and particle size, indicate that K_2 for a 4.5- μm dust should be about 8 times greater than the K_2 for a 13- μm dust at constant porosity. However, a more porous cake is typically formed with a smaller particle size, partially offsetting the particle-size effect. This explains why the K_2 values of the 4.5- μm dusts (shown in Figure 3) were only from about 1.2 to 2.5 times greater than the corresponding 13- μm dusts.

The results shown in Figure 3 can be related to the cohesive characteristics of the fly ashes by comparing the data with aerated and packed porosity measurements (Figures 4 and 5). Figure 4 indicates that both the aerated and packed porosity measurements correlate closely with K_2 for a constant velocity and for dusts with approximately the same particle-size distribution. It is evident, however, that the K_2 measurements can be significantly influenced by gas velocity which, therefore, must be included in

any attempt to predict K_2 on the basis of porosity measurements. Figure 5 shows the relationship between porosity and K_2 at constant velocity, but with two different particle sizes. These data indicate that porosity measurements can be used as a basis to predict K_2 , but only if velocity and particle size are also incorporated into a model. The three variables, along with possible interactions among them, suggest that much more work is needed to develop a predictive model for K_2 .

Another aspect of filter performance is bag cleanability, which is also dependent on the cohesive properties of the dust. The correlations imply that, for dusts of similar particle-size distributions, the dusts with the highest tensile strengths and porosities will form dust cakes with the lowest K_2 values. However, this is only true if the residual dust cake weight does not increase. If the tensile strength is high, bags may not be easily cleaned and high dust cake weights could result. Nevertheless, the measured tensile strength and porosity of a dust can be used to predict qualitatively pore-bridging ability and dust cake resistance, which are the main indicators of filter performance.

Figure 3. Effect of face velocity on K_2 for screen tests with baseline and conditioned Monticello fly ash.

Figure 4. Correlation between K_2 and packed or aerated porosity for 13- μ m MMD fly ash.

Figure 5. Correlation between K_2 and aerated or packed porosity for 13- μ m and 4.5- μ m MMD fly ash.

4.1.3 Horizontal Reentrainment Tests

Reentrainment tests were also conducted with a bench-scale test system designed to investigate particle reentrainment with flow parallel to the dust surface, as shown in Figure 6. Initial tests, in which the flow velocity across the dust layer was determined by the cross-sectional area of the 2.5-in by 2.5-in square duct, showed that detectable reentrainment did not occur for duct velocities smaller than 5 ft/s and the flowmeters and tubing could not handle higher flow rates. Therefore, to achieve higher velocities across the ash up to 50 ft/s, a gate was installed at either the beginning or middle of the ash layer, as shown in Figure 6. This configuration enabled testing over velocities for which significant reentrainment occurred.

For the initial tests with the gate configuration, the dust was placed in the bottom of a flow channel with a recessed ash holder, and the surface of the ash was smoothed with a knife edge so that the ash layer was flush with the wall of the flow channel. To determine reentrainment, respirable mass measurements were taken every two minutes up to a total test time of 8 minutes for a given velocity. After eight minutes, the velocity was increased and respirable mass measurements were taken every two minutes. The velocity typically ranged from 5 ft/s when initial reentrainment was detected, up to 35 ft/s when significant reentrainment occurred. Results showed a velocity of at least 5 ft/s was required to induce reentrainment (see Figure 7). At 5 ft/s, greater reentrainment was seen with a baseline ash compared to a conditioned ash. However, at higher velocities, a greater level of reentrainment was seen with the conditioned ash. This result was surprising because the particle-to-particle binding forces are greater for the conditioned ash, which would be expected to result in less reentrainment. The reasons for this difference may be related to the cake structure. The conditioned ash forms a much more porous structure and may have a rougher surface structure. The baseline ash, on the other hand, tends to pack easily, resulting in a smoother surface that is less susceptible to reentrainment at higher velocities. To remove this possible bias, the procedure was changed so that the final layer of ash was sifted through a sieve onto the surface and was not smoothed with a knife edge. With this procedure, the surface structure for both the conditioned and baseline ashes should have been similar.

After changing the procedure, baseline and conditioning tests were conducted with both Monticello and Big Brown fly ashes. Results from the individual tests are shown in Figures 8 through 11. At each velocity, four repeat tests were conducted to establish the variability of the data. Results in Figures 8 through 11 are presented with error bars that signify plus or minus one standard deviation in the data. The measured levels of reentrainment appeared to be well behaved and highly repeatable. In most cases, the reentrainment was very low at 5 ft/s, but increased by 3 to 4 orders of magnitude at 25 ft/s. The highest velocity before catastrophic reentrainment occurred (when large chunks of ash would break loose and the ash layer would quickly erode away) was 25 ft/s for the Monticello ash and 35 ft/s for the Big Brown ash. This indicates that the Big Brown ash is more cohesive than the Monticello ash, and is consistent with the higher

HORIZONTAL REENTRAINMENT TEST SYSTEM

Figure 6. Horizontal reentrainment test system.

Figure 7. Reentrainment results with ash layer smoothed over with a knife edge.

measured tensile strength of the Big Brown ash. A comparison of the reentrainment for the baseline and conditioned ashes for the Monticello tests is shown in Figure 12, and the comparison for the Big Brown tests is shown in Figure 13. For all cases, except the lowest velocity, the reentrainment is lower for the conditioned samples, which is expected if the particle-to-particle binding forces are increased with conditioning. For the lowest velocity of 5 ft/s, the data indicate slightly higher reentrainment for the conditioned samples, but the values are just above background levels and appear to be within the variability of the data, so no difference should be inferred.

A second configuration was tested in which the gate was placed over the middle of the ash tray (rather than at the start of the ash tray) to see if the gate location would significantly affect the level of reentrainment. Results of these tests, shown in Figures 14 and 15, indicate the same effects of velocity and conditioning on reentrainment, thus the gate configuration does not appear to bias the results. With both gate configurations, the effect of conditioning on reentrainment was more pronounced with the Big Brown ash, which, as stated earlier, is consistent with the tensile strength data.

One of the objectives for conducting the horizontal reentrainment tests was to determine the velocity at which reentrainment occurs, relating the reentrainment velocity to cohesive measurements and, ultimately, to the particle-to-particle binding forces. An approximate calculation of the

Figure 8. Reentrainment results for baseline Monticello fly ash with flow gate in front of ash layer.

Figure 9. Reentrainment results for conditioned Monticello fly ash with flow gate in front of ash layer.

Figure 10. Reentrainment results for baseline Big Brown fly ash with flow gate in front of ash layer.

Figure 11. Reentrainment results for conditioned Big Brown fly ash with flow gate in front of ash layer.

Figure 12. Comparison of reentrainment between baseline and conditioned Monticello fly ash with flow gate in front of ash layer.

Figure 13. Comparison of reentrainment between baseline and conditioned Big Brown fly ash with flow gate in front of ash layer.

particle-to-particle binding forces can be made as follows: Measured tensile strengths for baseline and conditioned fly ashes with a mass median diameter (MMD) of about $13\text{ }\mu\text{m}$ have ranged from about 0.1 to 20 g./cm^2 . Assuming monosized $13\text{-}\mu\text{m}$ spherical particles and simple cubic packing (corresponding to a porosity of 47.6%), there would be 590,000 particles in contact in one cm^2 of area. This corresponds to a particle-to-particle binding force of $1.7 \times 10^{-6}\text{ g}$, or $1.67 \times 10^{-8}\text{ N}$ for a dust tensile strength of 1 g./cm^2 . The actual particle-to-particle binding force is likely to be somewhat higher because porosity is typically greater than 47.6% and the pore structure will not result in a perfect packing arrangement. To reentrain a particle requires that the particle-to-particle binding forces must be overcome by a fluid drag force. For a $13\text{-}\mu\text{m}$ spherical particle, applying Stokes' law, the velocity at which the drag force is equivalent to a $1.67 \times 10^{-8}\text{ N}$ particle-to-particle binding force is 25 ft/s. This velocity is within the range of velocities for which significant reentrainment was noted. The actual conditions at the boundary layer, where the reentrainment occurred, are not known, but the Reynolds numbers for flow through the gate were well within the turbulent flow region. The most significant reentrainment tended to occur somewhat downstream from the gate and may have been influenced by turbulent eddies. Even though a laminar sublayer may exist at the dust surface, calculation of

Figure 14. Comparison of reentrainment between baseline and conditioned Monticello fly ash with flow gate over the middle of ash layer.

Figure 15. Comparison of reentrainment between baseline and conditioned Big Brown fly ash with flow gate over the middle of ash layer.

the exact drag force on the particles that were reentrained would be difficult because the exact location where the particles were initially at rest (in relation to the gate orientation) was not known, and turbulent conditions were present. Nevertheless, results indicate that fairly high velocities would be required to produce a Stokes' drag velocity of 25 ft/s to overcome a 1.67×10^{-5} N particle-to-particle binding force.

Note that velocities in the range from 5 to 25 ft/s are from 75 to 375 times greater than the common filtration face velocity of 4 ft/min used with pulse-jet baghouses. With a dust cake porosity of 50%, the actual velocity of the gas through the cake would be twice as great, but this is still 37 times smaller than the minimum velocity at which reentrainment was noted. This implies that particle reentrainment due to viscous drag within the bulk of a dust cake should not occur under normal filtration conditions because the velocities are too low. On the other hand, if velocities are greater than 5 ft/s, particle reentrainment is expected. One situation where local velocity can greatly exceed 5 ft/s is when pinholes develop. According to capillary flow calculations, the velocity through a 100- μ m diameter pinhole can be from 100 to 1000 times greater than the face velocity, or from 400 to 4000 ft/min (6.7 to 67 ft/s) for a typical face velocity of 4 ft/min (10). Therefore, once pinholes form beyond a critical diameter, it is difficult to bridge them again because of the potential for reentrainment along the edges. After bag cleaning, many of the larger pores are opened which can also result in localized high velocities. These pores must be quickly bridged again to

result in a high particulate-removal efficiency. Therefore, dusts with superior pore-bridging ability will obviously be collected with a better efficiency, and, if pore-bridging ability (or resistance to reentrainment) can be predicted from cohesive measurements, collection efficiency is also predicted from these measurements.

4.1.4 Conclusions from the Fine-Particulate Control Work

Ammonia and SO_2 conditioning can greatly improve the particulate collection efficiency and reduce the pressure drop of a fabric filter. While conditioning has been proven to be effective for a variety of coals, fabrics, and bag-cleaning methods, the basis for the amount of conditioning agents to be used is not well known. Tensile strength, porosity, pore-bridging ability, and reentrainment potential of baseline and conditioned fly ashes were measured to determine if they can be used as predictors of fabric filter performance. Although both tensile strength and porosity measurements correlate with pore-bridging ability and K_2 , for fly ashes of similar particle sizes, tensile strength correlates more strongly with the pore-bridging ability of the dust, and measured porosity correlates more strongly with the K_2 of the dust. This implies that, for the best prediction of filter performance, both measurements should be conducted. However, more work is needed to quantify the correlations and to generalize them for other dusts.

4.2 **Impact of Coal Combustion on Atmospheric Visibility**

To evaluate the impact of fine-particulate emissions from coal-fired combustion systems on atmospheric visibility, a literature review was conducted. In order to achieve this goal, the literature survey has been organized to answer the following questions:

1. What are the causes of visibility impairment in the atmosphere? (For example, what sizes and concentrations of fine particulates in the atmosphere will result in significant visibility impairment?)
2. What is the composition of the visibility-reducing, fine-particulate aerosol, and what are the major sources of these fine particles?
3. What is the contribution from coal combustion to visibility-reducing fine particles in the atmosphere?
4. How are pollutants removed from the atmosphere, and what is the role of atmospheric chemistry in the production of secondary aerosols?
5. How would reduction of SO_2 , NO_x , and fine-particulate emissions affect visibility?

4.2.1 Causes of Visibility Impairment

Reduction in visibility is the most immediately perceived effect of air pollution on the properties of the atmosphere; however, visibility is not easily defined by a single, directly measured parameter. Visibility monitoring indexes are usually divided into three groups: aerosol, optical, and scenic. Aerosol indexes include the particle-size distribution, composition, physical characteristics, and mass concentration of the atmospheric aerosol through which light passes. Optical indexes include

determination of the scattering, absorption, and extinction coefficients which characterize the ability of the atmosphere to alter the light passing through it. Scenic indexes include determination of visual range, contrast measurements, and documentation of the scene by photography. The visibility issue also includes human perception of scenic beauty and visual range and attempts to place a monetary value on the aesthetics of a scenic feature.

The transmittance of light through the atmosphere is attenuated by absorption and scattering by particles and gases. The extinction coefficient, b_{ext} , measures the total fraction of light that is attenuated per unit distance and is given by Equation 1:

$$b_{ext} = b_{sg} + b_{sp} + b_{ag} + b_{ap} \quad [Eq. 1]$$

where b_{sg} and b_{sp} are the light scattering coefficients of gases and particles, and b_{ag} and b_{ap} are the light absorption coefficients due to gases and particles. The extinction coefficient is usually expressed in units of reciprocal length.

Light scattering by gases (Rayleigh or natural blue-sky scatter by air molecules) is typically on the order of 10 to 12 Mm^{-1} . Rayleigh scattering decreases with altitude and is proportional to the air density. At sea level, Rayleigh scatter is approximately 13.2 Mm^{-1} at $0.52\text{-}\mu\text{m}$ wavelength, limiting visibility to about 296 km (184 miles). Nitrogen dioxide (NO_2) is the only gas present in significant quantities in the atmosphere that strongly absorbs light. It preferentially absorbs blue light, giving plumes a red, yellow, or brown color; however, the contribution of NO_2 to total extinction is usually minor. In a study of the brown haze which frequently plagues Denver, Colorado, NO_2 accounted for only 6% of the total extinction (17). Light scattering by particles is usually the largest component of extinction, except under extremely clean conditions when Rayleigh scatter predominates. Light scattering is primarily a function of the fine particles in the 0.1- to $2.0\text{-}\mu\text{m}$ size range, especially those with sizes comparable to the wavelength of visible light (0.4 to $0.7 \mu\text{m}$). These particles are more effective at scattering light per unit mass than larger particles. Light absorption, on the other hand, is dominated by particles of elemental carbon (in the form of soot). Watson and others found large differences among elemental carbon contents of exhausts from motor vehicles powered by unleaded, leaded, and diesel fuels (18). As expected, diesel-powered vehicles were a major source of soot; however, large proportions of elemental carbon also came from unleaded gas-powered vehicles operating under very cold conditions.

Light-scattering efficiency is also affected by the absorption of water at high relative humidities. The six major components of fine-particulate aerosol are sulfates (typically associated with ammonium and/or hydrogen cations), organics, elemental carbon, ammonium nitrate, soil dust, and water (19). Sulfates and organics are the major contributors to fine-particulate mass. Fine sulfates typically account for over half of the fine-particulate mass in the East and less than half in the West (19). Nitrate contributions to fine mass are significant only in the West. Usually over 90% of both sulfates and nitrates are present as fine mass.

Results from the California Aerosol Characterization Experiment (ACHEX) showed that the major contributors to the light-scattering coefficient in the South Coast Air Basin of California were sulfates, nitrates, and organics

(20). An investigation of the relationship between visibility and aerosols in California showed that Rayleigh scattering accounted for only about 5% of the total extinction in most areas (21). Absorption by NO_2 accounted for 7% to 11% of the total extinction throughout the state, with sulfates responsible for 40% to 70% of the total extinction in Los Angeles and San Diego and 15% to 35% in the remainder of the state. In addition, nitrates accounted for 10% to 40% of the extinction in northern California. Black (graphitic) carbon, a significant contributor to visibility reduction, was not specifically accounted for in this study. However, a study by Conklin and others estimated that absorption by black (graphitic) carbon was responsible for as much as 17% of the total extinction in downtown Los Angeles in the wintertime (22). The contributions of fine-particulate species to the extinction coefficient from the Denver Brown Cloud Study are given in Table 1 (17). As shown in the table, elemental carbon was responsible for nearly 40% of the total extinction in Denver in the winter.

The contribution of a compound to extinction is not necessarily proportional to its contribution to fine mass. It may contribute more or less than its mass concentration to visibility impairment depending primarily on its size distribution and refractive index. For example, soot is approximately three times more efficient than SO_4^{2-} , NO_3^- , or organics in terms of visibility reduction per unit mass (23).

Fluctuations in relative humidity can have a significant impact on light extinction by aerosols. Water affects visibility only when it is in the liquid or solid phase. However, it is difficult to directly measure the contribution of liquid water to fine-particulate mass because of its rapid phase change. Typically, less than 0.01% of all water in a given volume exists in the liquid phase (except in fogs). Relative humidities above 70% greatly reduce visibility by increased light scattering due to the growth in size of hygroscopic aerosol species such as ammonium sulfate and sea salt.

Covert and others collected data on the humidity dependence of light scattering for different aerosol types (24). They classified the aerosols by their general chemical nature into four groups: marine, sulfate, urban/photochemical smog, and background continental (clean air from the dry southwest desert or high plains areas). The humidity dependence of the light-scattering coefficient can be expressed as the ratio $b_{sp}(\text{RH})/b_{sp}(\text{RH} = 30\%)$. At 60% relative humidity, acid sulfate, marine, and urban or photochemical aerosols had a mean ratio of 1.1 to 1.2, while sulfate salts and continental background aerosols had a ratio of 1.05 to 1.1. At 80% relative humidity, the scattering increased by a factor of 1.6 to 1.9 for all aerosol types, except continental background, which had a ratio of 1.3 or less.

Visual range is the maximum distance at which a large black object can be seen against the horizon sky in the daytime. Airport visual range determinations by human observers are the largest source of visual range data. In practice, an observer records whether or not a set of targets at known distances can be seen. Because nonideal (nonblack) and/or poorly placed targets are sometimes used, care must be exercised when comparing human observations of visual range with instrumental measurements of visibility. Visual range data derived using nonblack targets must be corrected for nonzero intrinsic target brightness to obtain standard visual range. Human

TABLE 1

Fine-Particulate Contribution to the Extinction Coefficient
for the Denver Wintertime Aerosol

Fine-Particulate Species	Mean Percent Contribution to b_{ext}
$(NH_4)_2SO_4$	20.2
NH_4NO_3	17.2
Organic Carbon	12.5
Elemental Carbon Total (scattering, 6.5; absorption 31.2)	37.7
Other	6.6
NO_2	<u>5.7</u>
Total	100.0

observations of visual range at airports are scheduled to be replaced by forward-scattering monitors in the mid-1990s (25).

The relationship between visual range and extinction is given by the Koschmeider equation (Eq. 2), where x is the visual range and b_{ext} is the extinction coefficient.

$$x = \frac{3.912}{b_{ext}} \quad [Eq. 2]$$

The constant in the equation is based on a contrast threshold of 0.02. The contrast threshold is the smallest increment of contrast that can be detected by the human eye and varies from observer to observer. Values of 0.0077 to 0.06 have been reported for the contrast threshold, corresponding to a range of 2.8 to 4.9 for the value of the constant in the Koschmeider equation. Typically, a value of 0.02 is used for visual range calculations. The Koschmeider equation ignores the earth's curvature and assumes that the atmosphere is homogeneous. The equation also assumes a perfectly black target observed against an ideal white background. The equation is of limited usefulness under partly cloudy skies because it assumes equal illumination of all parts of the atmosphere in the horizontal plane.

4.2.2 Source Contribution to Visibility Impairment

Evidence exists for a background level of atmospheric aerosol based on ambient aerosol measurements in remote areas (especially in the southern hemisphere). Measurements of light scattering at Point Barrow, Alaska, and Mount Olympus, Washington, using an integrating nephelometer, agree in magnitude, and are also in agreement with other measurements of light-

scattering and turbidity made in remote locations (26). Values of the background aerosol levels estimated from measurements at remote locations, compilations of man-made and natural sources, and regression studies using tracers are presented in Table 2 for the eastern and western United States. Rayleigh scatter (46%), organics (22%), and water (19%) are the major contributors to natural extinction in the East. In the West, the major contributors to natural extinction are Rayleigh scatter (64%), soil dust (including coarse particles) (14%), and organics (11%) (19).

The best visibility occurs in the mountainous Southwest with a median visibility of greater than 110 km (70 miles). Annual median visibilities are less than 24 km (15 miles) east of the Mississippi and south of the Great Lakes. The difference in median visibility is partially caused by the higher ambient relative humidities, greater vegetation densities (conducive to the formation of secondary aerosols), and hygroscopic marine aerosols in the East (27). In a study of visibility observations of three distinct mountains at Blue Hill, Massachusetts, from 1889 to 1958, researchers attempted to determine whether visibility was ever as good in the East as it is presently in the Southwest (28). Although two peaks in haziness corresponded roughly with two peaks in combined coal and wood burning (1910-1920 and 1940-1950), they were unable to state conclusively that fossil fuel burning was responsible for the increased haziness because of the variability in the data.

A study of haze in Shenandoah National Park concluded that 78% to 86% of the extinction coefficient was of anthropogenic origin. Of the 14% to 22% from natural causes, sulfates and associated water contributed 3% to 11% to the extinction coefficient; organics, 5%; Rayleigh scattering, 5%; and crustal dust, 1% (29). The sulfate estimate was based on measurements in remote areas; however, the estimate of 11% (based on measurements in remote South Dakota) may be more of a background value than the contribution from natural sources due to the general sulfate contamination of the northern hemisphere. The estimate of 3% (from measurements in South America) may be more reasonable. All elemental carbon was assumed to be anthropogenic in origin, and a ratio of 1.5 to 1 was used for the anthropogenic organic/elemental carbon emission ratio in the estimate of the natural source contribution of organics. Due to uncertainties

TABLE 2
Natural Background Levels of Atmospheric Aerosols

	Average Concentration		
	East ($\mu\text{g}/\text{m}^3$)	West ($\mu\text{g}/\text{m}^3$)	Error Factor
Fine Particles ($<2.5 \mu\text{m}$)			
Sulfates as NH_4HSO_4	0.2	0.1	2
Organics	1.5	0.5	2
Elemental Carbon	0.02	0.02	2-3
Ammonium Nitrate	0.1	0.1	2
Soil Dust	0.5	0.5	1.5-2
Water	1.0	0.25	2
Coarse Particles ($2.5-10 \mu\text{m}$)	3.0	3.0	1.5-2

in carbon speciation and in the organic/elemental carbon ratio, the natural organic contribution could be as large as 10% if all measured carbon were organic and from natural sources. Using values of 3% and 10% for the sulfate and organic contributions, respectively, and a more reasonable value of 3% for Rayleigh scattering, results in a natural source contribution to the extinction coefficient of 12% to 17%.

As part of the 1987-1988 Denver Brown Cloud Study (30), coal-fired power plants in Denver were switched to natural gas at about 2-week intervals. Previous studies had implicated sulfates as a significant contributor to the Brown Cloud. It was anticipated that a 70% reduction in SO_2 as a result of fuel switching would result in a significant reduction in sulfates. However, the anticipated reduction in sulfates did not materialize. Sulfate showed no change between coal- and gas-burning periods despite a two fold reduction in SO_2 emissions. Long-range transport of air pollutants from the Pawnee power plant in northeast Colorado was identified as a source of secondary particulates, complicating observations in Denver, especially when average concentrations were considered. Therefore, researchers have suggested that the entire South Platte River basin and its complex meteorology must be considered as a source region for Denver air pollution.

After eliminating periods of potential transport from the Pawnee power plant, the data indicated a distinct reduction in sulfates during gas-burning periods (30). However, the change was small compared to other pollutant species concentrations, including nitrates and elemental and organic carbon. Sufficient data that were unaffected by transport from the Pawnee power plant were not available to identify the effect of individual sulfate sources. Moreover, during a number of severe pollution episodes, neither transport from Pawnee nor other coal-fired power plants could be identified as major contributors. Further understanding of the role of ground-based sources of precursors to the formation of the Brown Cloud await the availability of a complete chemical data set from the study.

A strike in 1967-1968 which closed copper smelters in the Southwest for 9 months provided an opportunity to study the relationship between smelter emissions and ambient sulfate concentrations. At the time of the strike, copper production accounted for over 90% of the SO_x emissions and less than 1% of the NO_x emissions and, therefore, affected visibility primarily through its contribution to sulfate loadings. During the strike, substantial decreases in sulfate occurred at Tucson, Phoenix, Maricopa County, White Pine, and Salt Lake City, all within 113 km (70 miles) of copper smelters. Sulfates also dropped by about 60% at the Grand Canyon and Mesa Verde National Parks, 325 to 500 km (200 to 300 miles) from the main smelter area in southeast Arizona. Phoenix experienced a large decrease in sulfate concentration which was accompanied by a substantial improvement in visibility.

A strike in July 1980 shut down 9 of 11 copper smelters in Arizona and New Mexico for three months. After studying sulfate emissions and ambient air levels before, during, and after the strike, researchers concluded that the largest sulfate concentrations at remote sites in Arizona and southern Utah from August 1979 to July 1980 were accompanied by wind trajectories from copper smelters. During the strike, mean sulfate concentrations throughout Arizona decreased 50% to 90% from the previous summer.

The Winter Haze Intensive Tracer Experiment (WHITEX) was designed to evaluate the feasibility of using various receptor modeling techniques to attribute emissions from a single point source, the Navajo Generating Station (NGS), to the visibility impairment in a number of national park areas, including the Grand Canyon (31). The NGS is a 2250-MW coal-fired utility plant located at Page, Arizona. Tracer mass balance regression (TMBR) analysis of data from the Hopi Point, Grand Canyon, monitoring site was used to estimate the contribution of the NGS to secondary sulfates and nitrates at the Grand Canyon. A tracer, deuterated methane (CD_4), was released from one of the three stacks at the NGS during the study. CD_4 is nonreactive and stable (even at elevated temperatures) with a presumed deposition velocity close to zero. It is not emitted by other sources and has a background concentration of 1 part in 10^{16} . Attempts to vary the tracer emission rate in proportion to the plant load were not very successful; therefore, the data were "standardized" to a constant CD_4 emission rate for analysis. Results from the study indicated that the NGS contributed from 70%-80% of the sulfate concentration at the Grand Canyon, with copper smelters contributing 10%-30% (30). Background sulfate concentration was estimated between 0% and 10%. Results from the Differential Mass Balance (DMB) Model, also used in the WHITEX study, found that NGS contributed 71% of the ambient sulfate measured at Hopi Point (32).

Based largely on the results of this study, the EPA has ruled that NGS must phase in scrubbers between 1997 and 1999, reducing the plant's SO_2 emissions 90% (33). This ruling marks the first, and perhaps only, time the EPA has acted solely to protect visibility in a national park.

4.2.3 Atmospheric Chemistry

The gas-phase conversion of SO_2 and NO_x to H_2SO_4 and HNO_3 is controlled by the concentration of the $\text{OH}^\cdot$ radical. The estimated residence time of SO_2 in the atmosphere has been reported to range from 4 to 40 days (34). The gas-phase conversion rate of SO_2 by the $\text{OH}^\cdot\text{SO}_2$ reaction varies from 0.7%/hr in the summer to 0.12%/hr under winter conditions. Assuming the same $\text{OH}^\cdot$ levels, conversion of NO_x to HNO_3 was estimated to vary from 6.2%/hr in the summer to 1.1%/hr in the winter (33). Sulfuric acid formed in the gas-phase immediately associates with water molecules to form sulfuric acid aerosol. Nitric acid remains as a vapor until it is absorbed by a cloud or raindrop or reacts with ammonia to form ammonium nitrate. Ammonium nitrate is present as particles only when equilibrium is achieved with ammonia and nitric acid gases in the environment. Conversion of SO_3 to sulfuric acid aerosol in the gas-phase depends primarily on the concentration of the $\text{OH}^\cdot$ radical. The concentration of the $\text{OH}^\cdot$ radical depends indirectly on the NO_x and hydrocarbon levels, as well as on sunlight intensity. The conversion of SO_2 by the $\text{OH}^\cdot$ radical is linear; however, it is influenced in a complex (most probably nonlinear) manner by the concentrations of NO_x and hydrocarbons and their effect on the $\text{OH}^\cdot$ concentration.

Additional sulfate is formed by the absorption of SO_2 by droplets of water, followed by aqueous-phase oxidation. The amount of SO_2 absorbed depends on the SO_2 concentration and on the pH of the solution. Hydrogen peroxide (H_2O_2) is a major aqueous-phase oxidant; however, its concentration in the atmosphere is typically only in the parts per billion (ppb) range. Therefore, in this case, the oxidation of SO_2 to sulfate may be limited by the concentration of H_2O_2 . Ozone (O_3) is also an effective oxidant; however, its

oxidation potential decreases rapidly as the pH decreases, suggesting that H_2O_2 may be a more effective oxidant. At the moderately acidic conditions normally found in atmospheric water droplets, dissolved SO_2 ionizes to bisulfite. This ion is then oxidized to sulfate by any of several oxidizers. It is believed that in-cloud oxidation of S(IV) to sulfate is dominated by H_2O_2 , because oxidation by O_3 is suppressed, particularly at the low pH levels typically found in cloud water droplets. Buffering agents such as NH_3 and carbonates from soil dust can raise the pH sufficiently for the oxidation of SO_2 by O_3 to occur. Ammonium sulfate is formed primarily by the reaction of ammonia with sulfuric acid.

In laboratory experiments on the gas-solid reaction of SO_2 with carbon, Novakov and others found that graphite and soot particles oxidize SO_2 in air (35). Soot exposed to humidified air in the presence of SO_2 produced more sulfate than soot exposed to dry air. They also found a correlation between ambient concentrations of carbon and SO_4 in Los Angeles, which supports their hypothesis that carbon (soot) oxidation may be an important pathway for sulfate formation. The catalytic formation of sulfate on soot particles may be of greatest significance in the open atmosphere, particularly near combustion sources where the concentrations of SO_2 and soot are both high.

Secondary particles formed from alkenes having seven or more carbon atoms (cyclic olefins, diolefins, and terpenes) produce considerable visibility impairment. For example, secondary organics produced from cyclic olefins and diolefins generally are in the 0.1- to 0.3- μm size range. Particle formation consists of supersaturation of the gas-phase and subsequent condensation on pre-existing particles. In Los Angeles, the average conversion of precursor organic vapors to organic particles was estimated to be 1% to 2%/hr.

Pollutants are removed from the atmosphere by dry and wet deposition. In dry deposition, the pollutant is absorbed at the surface of the earth by soil, water, or vegetation. Dry deposition is controlled by a number of processes, including turbulent mixing of the atmosphere and the chemical and biological interaction of the pollutant and the surface on which it is deposited. Wet deposition refers to absorption of the pollutant into water droplets and subsequent removal by precipitation. Wet deposition, therefore, is governed by cloud physics and gas- and liquid-phase chemistry. Dry deposition is characterized by the deposition velocity, v_d , which is defined as the ratio of the flux of the material to the earth's surface and the ambient atmospheric concentration of the species. The highest deposition velocities generally occur during the day when atmospheric mixing is the greatest and the leaf stomata of vegetation are open. Deposition velocities range from 0.1 to 2.3 cm/s for SO_2 , with a median value of 0.7 cm/s (32). Typical deposition velocities for fine particles range from 0 to 1.0 cm/s, with a median value of 0.2 cm/s. The dry deposition process for gases is influenced by many factors, including seasonal effects, diurnal effects (sunlight, atmospheric stability), and meteorological effects (humidity, wind speed, temperature).

4.2.4 Coal Combustion and Visibility

As is shown by the following discussion, secondary sulfates from coal combustion contribute significantly more to visibility impairment than primary fly ash emissions. Two scenarios are evaluated with a coal assumed to have

the following characteristics: higher heating value of 12,000 Btu/lb, 1.5% sulfur and 8% ash.

Scenario #1:

The facility has an ESP with a collection efficiency of 95% for particulate matter (PM) with no SO₂ scrubbing. The resulting emissions would then be 2.5 lb SO₂/10⁶ Btu and 0.27 lb PM/10⁶ Btu. The mass ratio (SO₂/PM) would then be 9.3.

Scenario #2:

In this case New Source Performance Standards must be met, which for this coal would be 0.6 lb SO₂/10⁶ Btu and 0.03 lb PM/10⁶ Btu. The mass ratio (SO₂/PM) for this case would be 20:1.

Assuming the MMD of the PM emissions is 5 μm (D_p) and 0.3 μm (D_s) for secondary sulfates, and since the number of particles for a constant mass is directly related to the cube of the particle diameter, the particle number ratio (D_p³/D_s³) is 4630. For scenario #1 there would be approximately 43,000 (9.3 x 4630) more secondary sulfate particles than other emitted particles. For scenario #2, the same calculation shows that there would be 93,000 (20 x 4630) more secondary particles emitted. This clearly shows that secondary sulfate particles are of primary concern.

4.2.5 Effect of Reduced Emissions on Atmospheric Visibility

Improved visibility should be an important indirect result of the reduction in SO₂ and NO_x required by the Clean Air Act Amendments. However, controlling SO₂ and NO_x emissions are not necessarily the only way to reduce ambient sulfate and nitrate concentrations. In parts of the western United States where the contribution of fine ammonium nitrate to visibility reduction is significant, perhaps controlling ammonia from cattle feedlots would be appropriate for reducing ambient nitrate levels. The ammonium ion is found predominantly in the optical-scattering size range or below. It is likely secondary in origin, produced by the neutralization of acid sulfate particles by ambient NH₃. Reducing urban ozone levels by controlling hydrocarbon and/or nitrogen oxide emissions may slow oxidation of SO₂ to sulfate, reducing ambient sulfate concentrations. Due to the complex processes which control the formation of secondary sulfates and nitrates in the atmosphere, controlling emissions of SO₂ and NO_x may not yield proportionate reductions in ambient sulfate and nitrate concentrations and a corresponding improvement in visibility.

As discussed earlier, the aqueous-phase oxidation of SO₂ to sulfate may be oxidant-limited. Therefore, at distances from the source where the molar concentration of SO₂ is greater than the molar concentration of H₂O₂, the wet deposition rate is a constant that depends on the oxidant concentration. At greater distances from the source where the SO₂ concentration is less than the oxidant concentration, the wet deposition rate becomes proportional to the SO₂ concentration as the distance from the source increases. Therefore, if emissions are reduced, the change in wet deposition rate will not be proportional to the change in emissions except at great distances from the source. Where the SO₂ concentration is greater than the oxidant concentration, the reduction in emissions will have no effect on the deposition rate. The formation of nitric acid is dependent on the level of photochemical activity in the atmosphere. Therefore, nitrate concentrations

may not respond linearly to a change in NO_x emissions depending on how the changes affect the OH level.

The regional impacts on visibility and acid deposition (RIVAD) model, a plume-segment Lagrangian model designed to evaluate regional source-receptor relationships, was used to evaluate the effects on regional visibility of a 12-million ton per year reduction in SO_2 emissions in the 31 eastern states (36). The model calculated time-dependent air quality impacts by tracking the transport, dispersion, chemical conversion, and deposition of SO_2 and NO_x emissions in a plume segment representing 3-hour emissions. Three-hour time steps in upper-air wind fields, precipitation fields, atmospheric stability, and mixing heights were used to describe regional meteorology. Diurnal and seasonal variations in SO_2 oxidation rates were calculated in the model using a chemical module consisting of 8 reactions.

In 1980 total SO_2 emissions in the 31 eastern states were estimated at 21.9 million tons, with power plants accounting for 74%. The total SO_2 emission inventory for North America was estimated at 31.8 million tons, with United States sources contributing 83% of the total and the 31 eastern states contributing 69%. A 12-million ton reduction in SO_2 emissions would result in reductions of 55% and 38% in SO_2 emissions for the 31 eastern states and the United States overall, respectively. Based on simple mass balance calculations, one would expect a corresponding reduction in SO_x concentrations. The RIVAD model improves on these estimates by accounting for the locations of sources and the time- and space-dependent meteorological patterns that affect the transport, dispersion, transformation, and deposition of SO_2 emissions.

Calculations based on the RIVAD model showed that in 1980 sulfate accounted for 30% to 70% of the annual average light extinction in the eastern United States. Sulfates accounted for 70% of the extinction in the Appalachian Mountains of Pennsylvania, Maryland, West Virginia, and Virginia. Other researchers have shown that sulfates and associated water account for approximately 50%, on average, of the light extinction that causes haze, and up to 75% of the light extinction in nonurban areas in the summer.

Regional reductions in sulfate concentrations from a 12-million ton reduction in SO_2 emissions range from approximately 30% to a maximum of 54%. Reductions of more than 50% occur in Kentucky, West Virginia, Virginia, Tennessee, and North Carolina. Most highly populated areas in the Midwest and Northeast would experience a reduction in sulfate concentrations of 40%-50%. These predicted sulfate concentrations are based on the assumption that regional sulfate concentrations are linearly related to SO_2 emissions. However, recent work has suggested that sulfate may be related nonlinearly to regional SO_2 emissions changes partially because the in-cloud oxidation of SO_2 may be limited by the pH-dependence of SO_2 solubility.

Regional SO_2 emission controls would improve visibility by reducing the contribution of sulfates to light extinction and the total light extinction. The visual range was calculated using the following equation:

$$r_v = \frac{3}{b_o + b_s}$$

where b_o is the light extinction due to fine-particulate aerosols other than sulfate, and b_s is the sulfate light-scattering coefficient. The authors chose to use 3 rather than 3.912 as the constant in the equation because they concluded that it gave better agreement between airport observations of visual range and light extinction. A constant of 3 is obtained when a contrast threshold of 0.05 rather than 0.02 is used.

The sulfate light-scattering coefficient, b_s , depends on relative humidity and on whether the sulfate exists as H_2SO_4 , $(NH_4)HSO_4$, or $(NH_4)_2SO_4$, due to the variable mass of liquid water and associated cations:

$$b_s = K f(RH) [SO_4]$$

where K is the scattering efficiency per dry mass of sulfate anion, $f(RH)$ is a dimensionless factor that accounts for the associated liquid water, and $[SO_4]$ is the concentration of the SO_4 anion.

The value of K depends strongly on the particle-size distribution. In this analysis, K was calculated from Mie theory using a mass median diameter of $0.3 \mu m$ and a geometric standard deviation 2.0 (a typical sulfate aerosol size distribution) and the sulfate species density ($1.8 g/cm^3$). The form of sulfate affects the value of K because of the difference in cation mass associated with the sulfate anion; $K=4.6$, 4.0 , and $3.4 m^2/g$ for $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and H_2SO_4 , respectively.

The value of $f(RH)$ depends strongly on the molecular form of sulfate and on the relative humidity. In nonurban areas of the eastern United States, sulfate typically exists as $(NH_4)HSO_4$, whereas in urban areas it exists as $(NH_4)_2SO_4$. The average and midday humidities in the East are 70% and 60%, respectively. The value of $f(RH)$ is 1.0 for $(NH_4)_2SO_4$, and 2.2 and 2.9 for $(NH_4)HSO_4$ at relative humidities of 60% and 70%, respectively. However, $(NH_4)_2SO_4$ can also have values in the range of 2.2 to 2.9 due to hysteresis. If $(NH_4)_2SO_4$ is cycled from a humidity above its deliquescence point (approximately 80% RH) due to diurnal changes during the day, or over a shorter time period as it is mixed from higher (colder) elevations, the aerosol exhibits hysteresis and does not reach its equilibrium water content but instead exists as a supersaturated droplet. Therefore, for a typical midday relative humidity of 60%, the lowest humidity (highest temperature) of a diurnal cycle, the overall light-scattering efficiency of ammonium sulfate could be significantly higher than the theoretical value of $4.6 m^2/g$.

Significant reductions in sulfate concentrations may tend to lower the light-scattering efficiency per unit mass as well as the sulfate mass. Therefore, a reduction in SO_2 emissions may have a greater than proportional effect on light extinction because of the simultaneous reduction in both the sulfate concentration and its light-scattering efficiency. If sulfate concentrations are reduced by a factor of 2 while ammonia concentrations remain constant, the regional average (nonurban) aerosol may change from $(NH_4)HSO_4$ to $(NH_4)_2SO_4$, decreasing the regional-average sulfate light-scattering efficiency from 8.8 to $4.6 m^2/g$. This decrease would occur only in nonurban areas since urban aerosol already exists as $(NH_4)_2SO_4$. However, if

hysteresis occurs, the reduction in scattering efficiency may not occur in urban areas either. Other factors, such as a shift in the sulfate aerosol size distribution, could also change the scattering efficiency of the atmosphere as regional SO_2 emissions are changed. Higher ambient NH_3 concentrations may result from a reduction in sulfate concentration, producing more nitrate aerosol from nitric acid vapor. The presence of a film of organics on the aerosol surface could affect the growth and scattering efficiency of the sulfate aerosol.

Due to uncertainties in the ammonium/sulfate ratio and the potential hysteresis effects associated with changing relative humidity, the authors considered the following three assumptions for the sulfate light-scattering efficiency in estimating regional visibility improvement:

1. Assume sulfate exists as $(\text{NH}_4)_2\text{SO}_4$ with a scattering efficiency of $4.6 \text{ m}^2/\text{g}$ (at 60% RH).
2. Assume sulfate exists as $(\text{NH}_4)\text{HSO}_4$ with a scattering efficiency of $8.8 \text{ m}^2/\text{g}$ (at 60% RH), or as $(\text{NH}_4)_2\text{SO}_4$ undergoing significant hysteresis associated with temperature and relative humidity cycling so that its liquid water content and scattering efficiency are higher than equilibrium values.
3. Assume sulfate exists initially as $(\text{NH}_4)\text{HSO}_4$ with a scattering efficiency of $8.8 \text{ m}^2/\text{g}$ (at 60% RH), and after SO_2 emissions controls, with sulfate effectively halved, as $(\text{NH}_4)_2\text{SO}_4$ with a scattering efficiency of $4.6 \text{ m}^2/\text{g}$.

Empirical evidence for the effect of hysteresis on sulfate light scattering lead the authors to use the second assumption to estimate regional visibility improvements resulting from SO_2 emissions control.

Model calculations of the percentage improvement in visibility resulting from a 12-million ton reduction in annual SO_2 emissions are given for a 31-state region in the eastern United States, and for the Ohio River Valley, where the existing visibility is the lowest and the predicted change in sulfate concentration is the highest. The calculations were performed assuming both a linear and nonlinear relationship between SO_2 emissions and sulfate concentration. The nonlinear relationship used assumed that a 50% reduction in SO_2 emissions would result in only a 35% reduction in the sulfate concentration. The percentage improvement in average annual visibility for the 31-state region was 26% assuming a linear relationship between SO_2 emissions and sulfate concentration and 18% assuming a nonlinear relationship. For the Ohio River Valley, the improvement in visibility was 35% assuming a linear relationship and 25% assuming a nonlinear relationship. The model predicted a 50% increase in average annual visibility in the Appalachian Mountains, where sulfates account for up to two-thirds of the existing light extinction. The most significant uncertainties in this analysis concern the possible nonlinearity in the SO_2 -sulfate relationship and the effect of hysteresis on the sulfate light-scattering efficiency.

4.2.6 Summary of Literature Review on Atmospheric Visibility

Visibility impairment in the atmosphere is primarily caused by light attenuation by fine particles ($<2.5 \mu\text{m}$). Secondary fine-particulate matter

formed in the atmosphere from SO_2 and NO_x precursors are a major source of these fine particles. Other major constituents of fine atmospheric particles are organics, elemental carbon, ammonium ion, soil dust, and water vapor. Water vapor contributes to visibility impairment primarily when the relative humidity is high enough to cause growth in the size of hygroscopic aerosols such as ammonium sulfate. Since coal combustion is a major source of SO_2 (and, subsequently, atmospheric sulfates), some visibility impairment must be attributed to coal combustion. Visibility impairment in the Grand Canyon by secondary sulfates and nitrates from the Navajo Generating Station is a case where the visibility impairment was specifically attributed to a coal-fired power plant. In response, the EPA has required that scrubbers be installed at the Navajo plant to correct this visibility impairment. However, the exact contribution of coal combustion to regional haze is generally not known, and the benefits to be derived from much stricter emission controls on coal-fired power plants are difficult to assess. It appears logical that if SO_2 and NO_x emissions from coal-fired power plants were reduced by 50%, there would have to be an eventual reduction of 50% of the sulfates and nitrates in the atmosphere that originated from coal combustion. However, because of the variable contribution to visibility impairment from coal combustion that might occur in a given location, the overall effect on visual range for that location might be small.

Results from this literature review indicate there is a complex relationship between emissions from coal combustion sources and visibility impairment, but that coal combustion may be a significant contributor in some cases.

4.2.7 Summary of Selected Literature Sources

Begley, S. "The Benefits of Dirty Air - Pollution May Negate the Greenhouse Effect," *Newsweek* 1992, 1, 54.

Researchers from seven universities and federal agencies have reported that the same pollutants responsible for acid rain may ward off global warming. It has been generally known for some time that sulfate aerosols reflect sunshine and act as cloud condensation nuclei, which reflect solar radiation back into space and result in cooling of the Earth. However, according to the latest research, this cooling is just about equal to the heating effect due to "greenhouse gases" such as CO_2 , and therefore likely offsets global warming to a large degree. Thus there has been less warming of the Earth than predicted by simple greenhouse models.

It has also been postulated that sulfates may defend the Earth against the disappearing ozone layer. A researcher at the National Oceanic and Atmospheric Administration (NOAA) has suggested that scattering of ultraviolet (UV) radiation by fine sulfate is the reason why, despite a 5% decrease in wintertime ozone in the northern hemisphere over the last decade, there is not much more UV radiation reaching the ground.

Burns, S.; Frey, S.J.; Chow, J.C.; Watson, J.G.; Sloane, C.S. "An Overview of the 1987-1988 Metro Denver Brown Cloud Study," In *Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 363-373.

This paper presents an overview of the design and methods used in the 1987-1988 Metro Denver Brown Cloud Study and a summary of the study results. The objectives of the study were to quantify the effect on extinction (particularly due to sulfates) when metro area coal-fired power plants were switched to natural gas, and to determine the contribution of all major sources to light extinction. In addition to fine particle, gaseous, visibility, and meteorological measurements, source characterization tests were performed to establish area-specific chemical source profiles. Categories included in the source apportionment included clean air, NO_2 , primary geological material, primary boilers, primary mobile source exhaust, primary woodburning, secondary ammonium sulfate, and secondary ammonium nitrate. Extinction efficiencies were estimated for sulfate, nitrate, elemental carbon, and organic carbon using linear regression and deterministic calculations. Source apportionment was determined by receptor modeling, using the chemical mass balance (CMB) model.

Approximately one-third of the NO_x emissions are from mobile sources, one-third from power plants, and the rest from space heating and other sources. Approximately 70% of the area's SO_2 emissions are from coal-fired power plants. Other sources include a brewery, refineries, and diesel engines. Although an ammonia emissions inventory has not been developed for the Denver area, it is likely that agricultural and biogenic sources are significant.

Organic and elemental carbon combined were the largest contributors to fine-particle mass ($<2.5 \mu\text{m}$), accounting for approximately 50% of the fine-particle mass. Nitrates accounted for 20% of the fine-particle mass and sulfate and ammonium each contributed approximately 8%. Sampling artifacts may have resulted in an overestimation of 15% in the organic carbon concentration and a 10%-20% underestimation of the nitrate concentration. On the average, 50%-60% of the light scattering was due to particle scattering, 24%-28% to particle absorption, 7%-12% to gas absorption, and 6%-8% to gas scattering. Elemental carbon had the largest light extinction efficiency ($9.1 \text{ m}^2/\text{g}$ at 50% RH). The extinction efficiency of ammonium sulfate was $4.3 \text{ m}^2/\text{g}$, and ammonium nitrate and organic carbon each had extinction efficiencies of $3.6 \text{ m}^2/\text{g}$. The extinction efficiencies of organic carbon, ammonium nitrate, and ammonium sulfate are humidity-dependent and increase by over 30% at high relative humidities ($>80\%$ RH). The light-extinction efficiency was $1.0 \text{ m}^2/\text{g}$ for geological dust and primary boiler emissions (fly ash) and $0.17 \text{ m}^2/\text{g}$ for NO_2 .

Fuel switching at metro area power plants occurred whenever a clearing of air pollution was predicted after storms or periods of high winds. Emissions inventory estimates indicated that SO_2 emissions were reduced by approximately 70%, and NO_x emissions were reduced by at least 10% during gas-burning periods. The reduction in SO_2 emissions as a result of fuel switching from coal to natural gas produced a proportional reduction in ambient SO_2 levels; however, a proportional reduction in ambient sulfate levels did not occur. Although the maximum extinction attributed to sulfates during coal- and gas-burning periods was $54 \pm 17 \text{ Mm}^{-1}$ and $26 \pm 8 \text{ Mm}^{-1}$, respectively, the differences were not measured over the entire study. Due to differences in meteorological conditions during coal- and gas-burning periods, it was not possible to evaluate the

impact of the two fuels on visibility unambiguously. Meteorological conditions associated with severe pollution episodes occurred more frequently during gas-burning periods. Also, emissions from a distant coal-fired power plant may have contributed to the sulfate levels measured during gas-burning periods.

Dietrich, D.L.; Molenaar, J.V.; Faust, J.F.; Watson, J.G. "Transmissometer Extinction Measurements in an Urban Environment," In *Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 374-383.

This paper describes the design, implementation, and operational application of the Optec LPV-2 long-range transmissometer which was used to continuously monitor the total light extinction during the 1987-1988 Metro Denver Brown Cloud Study. The extinction was measured along a 2.67-km sight path, 75 m above street level (midlevel of the haze layer during daylight hours) in downtown Denver. Total extinction is usually estimated from point measurements of light scattering and absorption by particles and gases. Direct measurements of total extinction with the Optec LPV-2 transmissometer compared favorably with two methods of estimating total extinction (from collocated independent point measurements), with correlation coefficients of approximately 0.9. The median extinction for the study period was 81 Mm^{-1} (standard visual range, SVR, of 48 km); however, hourly and daily extinction varied over a wide range. During a classic 5-day winter haze event, total extinction ranged from approximately 50 to 700 Mm^{-1} (SVR of 78 to 6 km). Total extinction ranged from 25 to 100 Mm^{-1} (SVR of 150 to 39 km) during periods which were relatively pollutant free. The Colorado Air Quality Control Commission adopted an extinction visibility standard of 76 Mm^{-1} (SVR of 51.5 km or 32 mi) based on the results of the study. If the extinction for a four-hour average anytime between 8 a.m. and 4 p.m. is greater than this standard, a high-pollution day is declared by the Colorado Department of Health. An Optec transmissometer was installed in Denver in January 1990 for measuring extinction relative to the standard.

"EPA Issues Final Rule Designed to Improve Visibility in Grand Canyon," *Journal of the Air and Waste Management Association* 1991, 41, 1496.

On September 18, 1991, the EPA issued a final rule consistent with an agreement reached between the Salt River Project (SRP) and several environmental groups headed by the Grand Canyon Trust and the Environmental Defense Fund and facilitated by the EPA, that will significantly reduce air pollution and improve visibility in the Grand Canyon. Under the rule, SO_2 emissions from the SRP-operated 2250-MW coal-fired Navajo Generating Station (NGS), one of the largest electric utilities in the country, will be reduced 90%. The haze in the Grand Canyon typically occurs in 2-5 day episodes and consists of a bright white layer with a distinct upper edge and occasionally one or more perceptible layers. The visibility impairment in the Grand Canyon is caused by a mixture of nitrates, sulfates, and dust particles. A 300% improvement in visibility is expected during the worst haze episodes and a greater than 7% average improvement is expected over the winter months (November-March) when there are increasing numbers of visitors to the Canyon. In 1989, approximately 900,000 people visited the Canyon in the winter, 21% of the annual total.

In February 1991, the EPA initially proposed a 0.30 lb per million Btu SO₂ emission limit for the NGS, a 70% reduction from currently allowable SO₂ emission levels. Under the rule issued in September, the emission limit was set at 0.10 lb of SO₂ per million Btu or a 90% reduction from current levels. The NGS will also shut down some of its units for maintenance during the winter months, when plant emissions contribute most to visibility impairment. Thus, the final rule provides tougher control at a lower cost than EPA's proposal, \$430 million instead of \$510 million. The levelized annual cost based on flue gas desulfurization using wet scrubbers, which the EPA considers the best control technology currently available, is \$90 million (1992 dollars). The controls will be phased in from 1997 to 1999.

Federal Register 1990, 55, 38403-38408.

The Department of the Interior has determined that the increase in emissions resulting from a proposed electric generating station by Multitrade Limited and other proposed facilities in Virginia is very likely to worsen the existing adverse visibility conditions at Shenandoah National Park and cause further perceptible visibility degradation. Therefore, it has recommended that the Virginia Department of Air Pollution Control deny a permit to Multitrade Limited for a major new emitting facility 110 km southwest of the park unless measures are taken to ensure that the proposed source will not contribute to adverse impacts on park resources.

As of September 1990, the Virginia Department of Air Pollution Control had recently granted permits for the construction and operation of four electric generating facilities, and applications for eleven other proposed facilities were in the review process. All fifteen of the facilities are within 200 km of Shenandoah National Park. The four permitted facilities have estimated SO₂, NO_x, and VOC emissions of 5988, 9512, and 475 tons per year, respectively. The estimated SO₂, NO_x, and VOC emissions from the other eleven proposed facilities (including Multitrade Limited) are 14,101, 26,792, and 115 tons per year, respectively. If all fifteen facilities were constructed and operated as proposed, statewide emissions of SO₂ and NO_x would increase by 7% and 22%, respectively, with even larger percentage increases in the vicinity of the park. Data from the Virginia Department of Air Pollution Control indicate that SO₂ and NO_x emissions would increase by 37% and 113%, respectively, for all point sources within approximately 100 km of the park boundary.

The estimated visual range in the eastern United States under natural conditions, without the influence of air pollution, is 150 ±45 km based on studies of historic visibility conditions. Sulfur has dominated the haziness over the eastern United States since the late 1940's. The estimated natural fine-particulate mass and natural sulfate concentrations in the East are 3.3 µg/m³ and 0.2 µg/m³, respectively. The annual average visibility in the southeastern United States declined 60% from 1948 to 1983, with a decline of 40% in the winter and 80% in the summer. The average visual range in rural areas of the East is currently 20-35 km, significantly less than the estimated visual range of 150 km under natural conditions. Sulfates are currently responsible for most of the visibility impairment in the East.

The National Park Service (NPS) has been monitoring visibility at the park since 1980. Data collected in 1988 and 1989 show that during the summer (June-September) the monthly average fine-particle concentration ranged from 19.5-28.9 $\mu\text{g}/\text{m}^3$, six to nine times higher than the estimated annual average natural background concentration. From June 1982 to May 1986, the summer average fine-particle mass concentration was 16 $\mu\text{g}/\text{m}^3$, five times the estimated natural background. The average concentration for the entire period was 10 $\mu\text{g}/\text{m}^3$, three times the estimated natural background.

Researchers have shown that sulfates are responsible for 70%-85% of the visibility impairment at Shenandoah National Park. The average summer sulfate concentration between 1982 and 1984 ranged from 8.5-10.2 $\mu\text{g}/\text{m}^3$, forty to fifty times the natural background. The annual average sulfate concentration between 1982 and 1986 was 5.8 $\mu\text{g}/\text{m}^3$, nearly thirty times higher than the natural background concentration. In the summer of 1989, the average sulfate concentration was 11.2 $\mu\text{g}/\text{m}^3$, and the 12-month average for Dec. 1988-Nov. 1989 was 6.4 $\mu\text{g}/\text{m}^3$. Organics are responsible for most of the remaining visibility impairment. Nitrate aerosols average less than 2 $\mu\text{g}/\text{m}^3$ and are typically responsible for less than 1% of the visibility impairment. Occasionally, nitrates make up 10%-20% of the fine particle mass and may significantly affect visibility.

The NPS visibility monitoring program has shown that, with respect to uniform haze, visibility at Shenandoah National Park is impaired by anthropogenic pollution 90% of the time. In fact, visitor surveys have shown that poor visibility is the single most frequent complaint by visitors to the park. Studies on human perception of visual air quality have shown that a 5% change in extinction (standard visual range) is the lower-bound threshold which would be noticeable by a sensitive observer. A 15% change in extinction represents the upper-bound threshold which should be noticed by a casual observer.

Teleradiometer (1980-1987) and transmissometer (since 1989) measurements show that the median visual range at the Shenandoah National Park ranges from 10-113 km, with a geometric mean (1987) of 65 km. Therefore, median visibility at the park is one-tenth to three-fourths of the estimated natural visual range of 150 km, with an average visibility approximately 40% of natural conditions on an annual basis. Visibility in the park exhibits a seasonal pattern, with the worst visibility in the summer when park visitation is highest. The average visibility in the summer months ranges from 10-36 km, less than one-fourth of the estimated natural visual range.

Research by the NPS has shown that both local (within 200 km) and long-distance sources contribute to the uniform haze at Shenandoah National Park. Source areas in Ohio, Kentucky, West Virginia, Indiana, Michigan, and Illinois, in addition to Virginia, have been estimated to contribute to the visibility impairment at the park under certain conditions.

Prior to the passage of the Clean Air Act Amendments, the EPA had estimated that SO_2 emissions in Virginia would more than double by 2010. The Clean Air Act Amendments are expected to result in a reduction in sulfur dioxide emissions of almost 50% in the eastern United States;

however, the EPA estimates that SO₂ emissions will continue to increase in Virginia despite the overall reduction in the East, particularly between now and 2005. The Department of the Interior has suggested that Virginia develop a statewide emissions control strategy to protect the air quality related values in Shenandoah National Park, including an offset program requiring greater than one-for-one emissions reductions elsewhere in the state to offset proposed emission increases from major new or modified sources. The emissions control strategy would also establish a time frame for determining maximum allowable levels of air pollution in the state (statewide emission caps).

Federal Register 1992, 57, 4465-4470.

Studies by the National Park Service (NPS) have shown that air pollution is adversely impacting visibility and other air quality related values (AQRVs) at Great Smoky Mountains National Park. Therefore, the Department of the Interior has recommended that the Tennessee Air Pollution Control Division, as well as permitting authorities in North Carolina, South Carolina, and Georgia, deny permits for major new sources within 200 km of the park unless steps are taken to ensure that these sources do not contribute to adverse impacts on the park. The Interior Department has recommended the development of an emissions control strategy to protect the AQRVs of Great Smoky Mountains National Park including greater than one-for-one emissions reductions elsewhere in the state to offset proposed emission increases from major new sources and a statewide Reasonable Available Control Technology requirement to control emissions from existing sources. The emissions control strategy would also include a provision setting a time frame for determining maximum allowable levels of air pollutants in the state. Statewide emissions caps would be the primary vehicle for achieving the maximum allowable levels. Separate action is currently pending on a proposed new boiler at the Tennessee Eastman facility in Kingsport, TN, which would increase NO_x emissions in the area by 1542 tons per year. Sampling by the NPS has shown that Great Smoky Mountains National Park receives the highest nitrate deposition of any monitored national park.

The estimated visual range in the eastern United States under natural conditions, without the influence of air pollution, is 150 ± 45 km based on studies of historic visibility conditions. Sulfur has dominated the haziness over the eastern United States since the late 1940's. The estimated natural fine-particulate mass and natural sulfate concentrations in the East are 3.3 µg/m³ and 0.2 µg/m³, respectively. The annual average visibility in the southeastern United States declined 60% from 1948 to 1983, with a decline of 40% in the winter and 80% in the summer. The average visual range in rural areas of the East is currently 20-35 km, significantly less than the estimated visual range of 150 km under natural conditions. Sulfates are currently responsible for most of the visibility impairment in the East.

The NPS has been monitoring visibility at Great Smoky Mountains National Park since 1984, initially using cameras and teleradiometers to determine visual range. From 1985 through 1987, fine-particulate samples were collected using stacked filter units (SFU). Since 1988, visibility at the park has been monitored as part of EPA's IMPROVE sampling network for class I areas. The visibility monitoring program has shown that,

with respect to uniform haze, visibility at Great Smoky Mountains National Park is impaired by anthropogenic pollution greater than 90% of the time, with sulfates responsible for 70%-85% of the visibility impairment. Organics are responsible for most of the remaining visibility impairment. Nitrate aerosols are typically responsible for less than 1% of the visibility impairment, with an average concentration of less than $3 \mu\text{g}/\text{m}^3$. On occasion nitrates comprise up to 10% of the fine-particle mass and may have a significant impact on visibility. Research by the NPS has shown that, in addition to local sources (those within 200 km), source areas in Ohio, Kentucky, West Virginia, Virginia, Indiana, North Carolina, and Illinois may also contribute to the haze obscuring the scenic views in the park.

The summer (June-September) average fine-particle concentration measured at the park from March 1988 to February 1991 using the IMPROVE sampler ranged from 8.7 to $25.1 \mu\text{g}/\text{m}^3$, three to eight times higher than the estimated annual average natural background concentration. Data obtained during the period from March 1985 to February 1987 using the SFU showed that the average summer fine-particle mass concentration was $9.3 \mu\text{g}/\text{m}^3$, three times the estimated natural background. The average fine-mass concentration for the entire period was $6.4 \mu\text{g}/\text{m}^3$, twice the estimated natural background. Analysis of the SFU data showed that the average summer sulfate concentration between 1985 and 1987 ranged from 1.9 - $8.3 \mu\text{g}/\text{m}^3$, ten to forty-two times the natural background concentration. The average annual sulfate concentration over the 1985-1987 time period was $4.9 \mu\text{g}/\text{m}^3$, almost twenty-five times higher than the natural background. The IMPROVE data were slightly higher than, but consistent with, the SFU data. The IMPROVE data show that the average summer sulfate concentration from 1988 to 1990 was $9.4 \mu\text{g}/\text{m}^3$, and the average sulfate concentration from March 1988 through February 1991 was $5.7 \mu\text{g}/\text{m}^3$.

The median visual range at Great Smoky Mountains National Park is 39 km, with a median summertime visual range of 19 km. Thus, visibility at the park has decreased to less than one-fourth of the estimated natural visual range. Visibility conditions at the park are strongly dependent on the season, with the worst visibility in the summer when park visitation is the highest. The average visibility in the summertime ranges from 23-43 km, which is less than one-third of the estimated natural visual range.

Flocchini, R.G.; Cahill, T.A.; Eldred, R.A.; Feeney, P.J. "Particulate Sampling in the Northeast: A Description of the Northeast States for Coordinated Air Use Management (NESCAUM) Network," In *Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 197-206.

A description of the Northeast States for Coordinated Air Use Management (NESCAUM) sampling network is presented. The NESCAUM network consists of seven regionally representative rural sites in eight states from Maine to New Jersey. The objective of the network is to define regional patterns of ambient fine-particulate matter.

Hameed, S.; Dignon, J. "Global Emissions of Nitrogen and Sulfur Oxides in Fossil Fuel Combustion 1970-1986," *Journal of the Air and Waste Management Association* 1992, 42, 159-163.

Estimates of global NO_x and SO_x emissions due to fossil fuel combustion are presented on a year by year basis from 1970 to 1986. The estimates are based on statistical models of the relationships between emissions and rates of fuel consumption. Nitrogen oxide emissions varied linearly with total fuel consumption and SO_x emissions exhibited a bilinear dependence on the rates of consumption of solid and liquid fuels. Estimates of the geographical distribution of NO_x and SO_x emissions for 1986 are presented on a latitude-longitude grid (with a resolution of 4.5° in latitude and 7.5° in longitude) which are suitable for use in global circulation models for three-dimensional simulations of atmospheric chemistry.

Emissions of total global NO_x increased by one-third, from 18 million tons N in 1970 to 24 million tons N in 1986. The average rate of increase from 1970 to 1986 was 1.8% per year, which is less than the historical rate of increase of 3.4% per year. Global NO_x emissions remained steady from 1977 to 1982 due to decreasing emissions in Europe and North America which offset increasing emissions in Asia and the USSR. In 1986, the five largest emitters of NO_x , in order, were the U.S., USSR, China, Japan, and West Germany. NO_x emissions in the United States peaked in 1979 and declined during the 1980s.

Global emissions of SO_x increased by approximately 18%, from 57 million tons S in 1970 to 67 million tons S in 1986. Emissions of SO_x declined steadily from 1973, excluding small increases in 1977 and 1984. European emissions fluctuated, with 1986 emissions nearly the same as in 1970. Asian emissions nearly doubled between 1975 and 1986, due primarily to an increased use of coal combustion in China, where the largest percent increase in SO_x emissions occurred (67%). Sulfur oxide emissions in China increased from 6 million tons S in 1970 to 10 million tons S in 1986. The five largest emitters of SO_x in 1986 were the USSR, U.S., China, India, and Poland.

Hanson, D. "Haze Obscuring Grand Canyon to be Reduced," *Chemical and Engineering News* 1991, 69, 7.

An agreement that should reduce the haze obscuring the view at the Grand Canyon has been reached by the Grand Canyon Trust, a conservation group, and the Salt River Project (SRP), an Arizona public utility and operator of the 2250-MW coal-fired Navajo Generating Station (NGS). Studies by the EPA in the 1980s and by the utility itself in 1990 showed that 40% to 60% of the sulfur dioxide in the fine particulates during the worst haze episodes came from the NGS. The Grand Canyon is the only area where the EPA has been looking at visibility standards. Therefore, this is the first, and probably only, time the EPA will act solely to protect visibility in a national park.

In February 1991, the EPA proposed a 70% reduction in SO_2 emissions at a cost of \$106 million a year. Under the new EPA-approved agreement, emissions will be reduced 90% at an annual cost of \$90 million. The savings result from changing the way in which the averaging time is

calculated for meeting the lower emissions level. The EPA-proposed plan used a 30-day averaging time which would have required extensive backup equipment. The new plan uses an annual rolling average, cutting the equipment cost 30%. The plant currently emits approximately 1 lb of SO₂ per million Btu. This will be reduced to 0.1 lb of SO₂ per million Btu using wet scrubbers. By 1999, when the controls are fully in place, the annual levelized cost could be reduced by more than \$35 million/yr through the sale of credits for the removal of 63,000 tons/yr of SO₂ earned under the revised Clean Air Act's SO₂ allowance-trading program. The credits should be worth approximately \$570 per ton of SO₂.

Miller, D.F.; Flores, M. "Sulfur Dioxide Concentrations in Western U.S.," *Atmospheric Environment* 1992, 26A, 345-347.

Weekly integrated SO₂ concentrations are presented for national parks in the western U.S., northern Minnesota, Alaska, and Hawaii for the period November 1986 to October 1987. The highest and most variable concentrations were measured at Hawaii Volcanoes National Park due to the activity of the Kilauea Volcano. Concentrations varied from 0.04 $\mu\text{g m}^{-3}$ (the minimum detection level) to 179 $\mu\text{g m}^{-3}$, with an annual mean SO₂ concentration of 30 $\mu\text{g m}^{-3}$. The SO₂ concentrations in Voyageurs National Park, MN, and the five parks in the western contiguous states were similar and ranged from 0.83 to 1.64 $\mu\text{g m}^{-3}$; the grand mean was 1.3 $\mu\text{g m}^{-3}$. The SO₂ concentration typically ranges from 0.1 to 0.15 $\mu\text{g m}^{-3}$ over the Pacific Ocean and from 5 to 50 $\mu\text{g m}^{-3}$ in the eastern United States.

Novakov, T.; Chang, S.G.; Harker, A.B. "Sulfates as Pollution Particulates: Catalytic Formation on Carbon (Soot) Particles," *Science* 1974, 186, 259-261.

This paper describes laboratory experiments on the gas-solid reaction of SO₂ with carbon. Electron spectroscopy for chemical analysis (ESCA) confirmed that both graphite and soot particles oxidize SO₂ in air. More sulfate was produced when the soot was exposed to humidified air than when it was exposed to dry air. Only low, background level peaks were produced when dry and humidified N₂ was used. The experiments also showed that soot-catalyzed oxidation of SO₂ occurred in the presence of flames and combustion-produced gases.

They also found a correlation between ambient concentrations of carbon and SO₄²⁻ in Los Angeles, which supports their hypothesis that carbon (soot) oxidation may be an important pathway for sulfate formation. The catalytic formation of sulfate on soot particles may be of greatest significance in the open atmosphere, particularly near combustion sources, where the concentrations of SO₂ and soot are highest.

Ondov, J.M.; Kelly, W.R. "Tracing Aerosol Pollutants with Rare Earth Isotopes," *Analytical Chemistry* 1991, 63, 691A-697A.

The authors describe the use of enriched stable isotopes of rare-earth elements to definitively track the movement of fine particles emitted from a specific source (or sources) and to determine how much material is deposited at a particular location. Enriched rare-earth tracers are applicable in the study of dry particle deposition and other

atmospheric phenomena. Enriched isotopes of Sm have recently been used in an EPA study to determine the contributions of residual heating oil combustion and diesel motor vehicles to airborne mutagens.

Particulate tracers with the power of inert gas tracers (such as deuterated methane and perfluorocarbon tracers used to study plume dispersion and transport) are essential in the study of the role SO_2 , NO_x , and particulates and the secondary aerosols formed from them play in the atmosphere. Enriched stable rare-earth elements are well-suited as particulate tracers because they are nontoxic, chemically stable, nonradioactive, and relatively inexpensive. They can withstand high-temperature combustion environments and are detectable with an ultimate sensitivity of 1 part in 10^{15} (mass of tracer to mass of air).

Rare-earth isotopes are particularly useful because the relative abundances of most rare-earth isotopes are nearly constant in nature and can be measured with great precision by thermal ionization mass spectrometry (TIMS). Therefore, instead of elevating the atmospheric concentration of the rare-earth element by an amount suitably in excess of its variability, it is only necessary to perturb the abundance ratio. Because the natural isotopic ratios are invariant, temporal or spatial biases arising from variations in the background concentration of the tracer element in the aerosol and reagents used in the analysis are eliminated. For example, neodymium has seven stable isotopes ranging in mass from 142 to 150. The background concentration of naturally occurring Nd can be determined simply by measuring one of the six other unperturbed Nd isotopes. In addition, several sources can be tagged simultaneously, each with a different isotope, and the relative and absolute contributions of each source can be determined in a single sample by its unique isotopic signature.

Application of the technique involves injecting enriched isotopes of rare-earth elements into the flue gas or fuel of a high-temperature combustion source and then measuring the perturbations of the natural isotopic ratios in aerosol particles collected in airsheds influenced by the source. Preliminary calculations using a multicomponent aerosol dynamics computer code, MAEROS, suggested that tracer particles <10 nm in diameter would be needed for quantitative scavenging by power plant particles under conditions expected in typical coal-fired power plants. Various particle generation techniques, including air-atomizing nozzles and a condensation technique were tested and optimized in the laboratory, and then field-tested at a small coal-fired utility boiler to determine if the tracer was actually becoming attached to the fly ash particles. In the field test, the tracer was injected near the inside wall of the duct work at the outlet of an air preheater. Despite passing through an induced-draft fan with a large reduction in volume, the tracer did not become well-mixed throughout the duct. Therefore, interpretation of the data was difficult because tagged fly ash was mixed with untagged fly ash and unattached tracer particles at the sampling location.

A technique was developed in which the 2,2,6,6-tetramethyl-3,5-heptanedione chelates of enriched Nd isotopes were vaporized and then degraded in the presence of fly ash. This technique delivered approximately 70 times more tracer than using a single nozzle atomizer. The vaporization technique was used to release ^{148}Nd in an urban-scale

test outside Washington, D.C. Aerosol samples were collected at 13 sites along a 72° arc located 20 km from a 100-MW coal-fired utility boiler. The tests were successful in that the signal-to-noise ratios were in good agreement with predictions for various particle size ranges. Measured tracer concentrations in ambient air agreed (within a factor of 3) with concentrations estimated from the release rate and plume dispersion calculations, except for 2 sites where sample contamination occurred.

Richards, L.W.; Anderson, J.A.; Blumenthal, D.L.; McDonald, J.A.; Bhardwaja, P.S.; Candelaria, R.B.; Moon, D.W. "Nitrogen and Sulfur Chemistry and Aerosol Formation in a Western Coal-Fired Power Plant Plume," In *Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 242-259.

Results are presented from airborne sampling in the vicinity of the Navajo Generating Station (NGS) at Page, Arizona, during the August 1980 Source Emission and Plume Characterization (SEAPC) Study. The SEAPC Study was conducted to obtain measurements of the rate of formation of sulfate and light-scattering particles in the NGS plume over a range of relative humidities. Plume chemistry, aerosol, and plume dispersion data were collected at distances of up to 140 km from the power plant.

The SEAPC study complements data obtained from the 1979 EPA/SRP (Salt River Project) sponsored Visibility Impairment due to Sulfur Transport and Transformation in the Atmosphere (VISTTA) Studies. The VISTTA data were obtained during periods of low relative humidity. During the VISTTA Study, the sulfate formation rates were about ten times smaller than expected and the secondary particles produced were too small to scatter light effectively. Aerosol formation was delayed until the emitted nitric oxide (NO) was oxidized to nitrogen dioxide (NO₂) by the ozone in the background air. EPA review of existing data on the formation of sulfate in plumes indicated that the VISTTA data were outliers. Another unusual result from the VISTTA Study was that essentially no fine-particle sulfate was emitted by NGS. Typically, sulfate formation is delayed until the plume is quite dilute. Thus, due to the emphasis on measurement of the optical properties of the NGS plume near the source during VISTTA, very few data points were obtained for sulfate and aerosol formation in the NGS plume under summertime conditions at distances where sulfate would likely form.

Results from SEAPC indicated that the NGS plume usually remained concentrated enough at distances of 50 km or more to contain significant amounts of NO which had not yet been converted to NO₂ by the background ozone. The authors believe that the persistence of unreacted NO and the accompanying depression of the ozone concentration contributed significantly to the slow initial oxidation rates for NO₂ and sulfur dioxide. Nitric acid was formed in the plume, but particulate nitrate was not. The ammonia gas concentration was so small that the nitric acid formed in the plume was not concentrated enough to saturate the plume with respect to the formation of solid ammonium nitrate. On the average, ammonium concentrations were 60% of those necessary to completely neutralize the sulfate and nitrate in the aerosol.

Size distributions were determined for both the primary aerosol (fly ash) and secondary aerosol (sulfates formed in the plume). On the day

with the lowest relative humidity (21%) during the study, the plume aerosol size distribution showed little or no formation of secondary (accumulation mode) aerosol; however, the primary (fly ash) emissions were clearly evident in the size range larger than approximately $0.5 \mu\text{m}$. On a day when the relative humidity was 83% at the start of the flight and averaged 77% during the sampling pass, formation of secondary aerosol was greatly accelerated. The secondary aerosol formed under conditions of higher humidity was capable of scattering light more effectively than sulfate formed at lower humidities.

Results from SEAPC indicated that conversions of SO_2 to sulfate were typically only a few percent; for example, at a distance of 140 km only 6.4% of the sulfur dioxide was converted to sulfate. As shown by VISTA, little formation of sulfate, nitrate, and light-scattering aerosol occurred during the first 70 km of plume travel. The largest sulfate formation rate observed in SEAPC was 1.6% per hour, which is only about one-third as large as typically observed in other studies. In the daytime, NO_x was oxidized to nitric acid approximately five times faster than SO_2 was oxidized to sulfate at low to moderate relative humidities in the dilute plume. It is believed that sulfate formation is very slow at night; however, nitrate formation occurs in the dark at an appreciable rate (in the presence of ozone). Ozone and NO_2 react to form NO_3 , and then N_2O_5 , which is hydrolyzed to nitric acid. These reactions do not occur at night because NO_3 is both photolyzed and destroyed by NO .

Robinson, E.; Robbins, R.C. "Gaseous Sulfur Pollutants from Urban and Natural Sources," *Journal of the Air Pollution Control Association* 1970, 20, 233-235.

Estimates of natural and anthropogenic sulfur emissions are presented, along with a discussion of scavenging processes. Natural sources of sulfur emissions are sulfate aerosols produced in sea spray and H_2S from the decomposition of organic matter and minor amounts from volcanic activity. Sulfur dioxide emissions are almost exclusively of anthropogenic origin. The total estimated annual emissions of SO_2 based on 1965 world data were 146 million tons. Of the SO_2 emissions, 70% resulted from coal combustion, 16% from the combustion of petroleum products (mainly residual fuel oil), and the remainder from petroleum refining and nonferrous smelting. Sources in the northern hemisphere were responsible for 93% of the total SO_2 emissions. Emissions of SO_2 were 69 million and 78 million tons in 1937 and 1940, respectively. Thus worldwide emissions of SO_2 nearly doubled between 1940 and 1965.

Hydrogen sulfide is rapidly oxidized to SO_2 in the troposphere by heterogeneous reaction on aerosol particles. The lifetime of H_2S ranges from approximately two hours in urban areas to two days in remote unpolluted areas. The solubility of SO_2 in water droplets with low pH is small; however, the aqueous oxidation of SO_2 may be promoted by the absorption of ammonia from the atmosphere which neutralizes the acid formed. A significant scavenging mechanism for SO_2 is the photochemical oxidation of SO_2 in mixtures with NO_2 and hydrocarbons. Once SO_2 and H_2S are in aerosol form as SO_4 , precipitation scavenging by clouds and rain is an effective removal process. Sulfur dioxide is also scavenged from the atmosphere by vegetation. The deposition velocity of SO_2 calculated from chamber studies is approximately 1 cm/sec.

Background concentrations of H_2S , SO_2 , and SO_4 were estimated from measurements in remote areas and used to estimate the environmental sulfur cycle (based on available data) which indicates a net transfer of sulfur from land to ocean areas. Estimates of the background concentration of SO_2 range from less than 0.3 ppb to 1 ppb. The background SO_4 concentration was estimated at $2 \mu\text{g}/\text{m}^3$.

Sloane, C.S.; Watson, J.G.; Chow, J.C.; Pritchett, L.; Richards, L.W. "Size Distribution and Optical Properties of the Denver Brown Cloud," In *Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 384-393.

The Micro-Orifice Uniform Deposit Impactor (MOUDI) was used to determine mass as a function of particle size (eight size ranges less than $1.8 \mu\text{m}$) for sulfate, nitrate, organic and elemental carbon during the 1987-1988 Denver Brown Cloud Study. Particulate mass was also simultaneously measured using teflon membrane and quartz fiber filters in a modified sequential filter sampler (SFS). The two methods of measurement were in good agreement for sulfate, nitrate, total carbon, and fine-particle mass. Comparison of the MOUDI and SFS organic carbon measurements indicated that the organic carbon measurements from the SFS quartz fiber filters were substantially positively biased. Analysis of fresh and aged fine-particle modes indicated that agricultural emissions of ammonia from areas northeast of Denver contribute significantly to the formation of fine ammonium nitrate in Denver. However, the small number of measurements from genuine episodes of visibility impairment, and the lack of a thorough ammonia emissions inventory for the Denver airshed, prevent a conclusive determination of the degree ammonia emissions control the formation of fine ammonium nitrate in Denver.

Sulfate had the largest light-scattering efficiency, followed by nitrate and organic carbon. The light-scattering efficiency of soot (elemental carbon) was much lower than that of the other chemical constituents. However, elemental carbon is much more efficient at light-absorption than the other principal species. The authors concluded that meteorological conditions that produce episodes of visibility impairment in Denver can be distinguished by the associated fine-particle-size distributions. Thus the light-scattering efficiencies of the principal chemical constituents are not constants.

"Smoky Mountains: More Controls Needed," *Air and Water Pollution Control* 1992, 5, 8.

Visibility impairment and other air pollution-related problems in the Great Smoky Mountains National Park have resulted in a recommendation by the Interior Department that new permit applications for air pollution sources near the park be denied. The Department has recommended that the Tennessee Air Pollution Control Division, as well as air permitting authorities in North Carolina, South Carolina, and Georgia, deny permits for major new sources within approximately 200 km (120 miles) of the park unless steps are taken to prevent further impacts on the park. Studies by the Interior Department have shown that fine particulate concentrations in the Smoky Mountains are three to eight times higher than the estimated annual summer natural background concentration. The Interior Department suggested that the states surrounding the park

develop an emissions control strategy, which might include greater than one-for-one emissions reductions elsewhere in the region to offset proposed increases in the area near the park.

The recommendation cannot, by itself, stop the issuance of permits; the final decision rests with the appropriate state agencies. Despite the same recommendation by the Interior Department in September 1990 for the Shenandoah National Park in Virginia, several new permits have been issued, and Virginia is considering a proposal for a new power plant on the edge of the park.

Thomas, J.; Parrott, H.; Yost, G. "Visibility Conditions in Eastern Wildernesses," In *Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 343-349.

Standard visual range (SVR) data are presented for spring, summer, and fall at four wilderness areas that are part of the Eastern Region of the Forest Service: Boundary Waters Canoe Area in Minnesota; Dolly Sods Wilderness in West Virginia; Lyle Brook Wilderness in Vermont; and Great Gulf Wilderness in New Hampshire. SVRs were estimated from photographs using scanning densitometry. The objectives of the visibility monitoring are: (1) to establish a record of visibility trends in Eastern Region Class I areas, (2) to improve effectiveness in responding to visibility analysis sections in prevention of significant deterioration (PSD) permit applications, and (3) to determine if visibility impairment exists in Class I areas. The best visibility occurred at Boundary Waters Canoe Wilderness Area for all three seasons. The visibility ranged from 90-250 km on most days. The smallest SVRs occurred at Dolly Sods Wilderness Area, with median visibilities on most days between 10 and 60 km. Visibility conditions at Great Gulf and Lyle Brook Wilderness Areas were similar; however, visibility was more variable at Great Gulf. Most summer and fall days at Lyle Brook had median SVRs that ranged from 10-70 km and 80-150 km.

Wolff, G.T. "Visibility-Reducing Species in New England's Berkshire Mountains," In *Visibility Protection: Research and Policy Aspects*; Bhardwaja, P.S., Ed.; TR-10, APCA, Pittsburgh, PA, 1986; pp 453-460.

Measurements of the fine-particle composition ($<2.5 \mu\text{m}$) and light-scattering coefficient were included as part of an intensive air quality and acid deposition study in the Berkshire Mountains of western Massachusetts in the summer of 1984.

Zurer, P. "Ozone Depletion: Arctic Hole Feared; Sulfate Aerosol Blamed," *Chemical and Engineering News* 1992, 70, 4-5.

Record amounts of chlorine monoxide (ClO) were measured over Canada and northern New England during January flights of the second Airborne Arctic Stratospheric Expedition (AASE-II). Chlorine monoxide is a free radical that accelerates ozone depletion. New data, from the study, document for the first time that reactions of nitrogen oxides on sulfate aerosol particles reduce the rate at which the atmosphere can recover from chlorine-catalyzed ozone destruction. Scientists have confirmed that the subtle but accelerating loss of ozone in the mid-latitudes, as shown by satellite observations over the last decade, is catalyzed by

chlorine and bromine free radicals. The study also revealed surprisingly low amounts of nitrogen oxides. Nitrogen oxides slow the rate of ozone depletion by tying up reactive chlorine and bromine as less reactive nitrates. The observations confirm the hypothesis, which was based on laboratory observations and computer calculations, that heterogeneous reactions on sulfate aerosols use up reactive nitrogen and thus accelerate ozone loss. Measured concentrations of nitrogen oxides were low (due to reactions on aerosol particles) as far south as the mid-Caribbean.

5.0 REFERENCES

1. Weber, G.F.; Collings, M.E.; Schelkoph, G.L. "Simultaneous SO_x/NO_x Control," Final Technical Report for the Period April 1, 1987, through March 31, 1988; DE-FC21-86MC10637, Grand Forks, ND, May 1988.
2. Weber, G.F.; Collings, M.E.; Schelkoph, G.L.; Steadman, E.N. "Simultaneous SO_x/NO_x Control," Final Technical Report for the Period April 1, 1986, through March 31, 1987; DE-FC21-86MC10637, DOE/FC/10637-2414, Grand Forks, ND, April 1987.
3. Weber, G.F.; Laudal, D.L. " SO_x/NO_x Control - Catalytic Fabric Filtration for Simultaneous NO_x and Particulate Control," Final Technical Report for the Period April 1, 1988, through June 30, 1989; DE-FC21-86MC10637, Grand Forks, ND, August 1989.
4. Miller, S.J.; Laudal, D.L. "Real-Time Measurement of Respirable Particulate Emissions from a Fabric Filter," In *Particulate and Multiphase Processes, Vol. 2, Contamination Analysis and Control*; Ariman, T., Ed.; Hemisphere Pub. Corp., 1987; p 663.
5. Miller, S.J.; Laudal, D.L. "Particulate Removal Enhancement of a Fabric Filter Using Flue Gas Conditioning," Presented at the Third EPRI Conference on Fabric Filter Technology for Coal-Fired Power Plants, Scottsdale, AZ, November 19-21, 1985.
6. Laudal, D.L.; Miller, S.J. "Flue Gas Conditioning for Improved Baghouse Performance," In *Proceedings of the Sixth Symposium on the Transfer and Utilization of Particulate Control Technology*; EPRI CS-4918, November 1986, Vol. 3, p 14-1.
7. Miller, S.J.; Laudal, D.L. "Flue Gas Conditioning for Improved Fine Particle Capture in Fabric Filters: Comparative Technical and Economic Assessment," In *Low-Rank Coal Research Final Report, Vol. II, Advanced Research and Technology Development*; DOE/FC/10637-2414 (DE87006532), April 1987.
8. Miller, S.J.; Laudal, D.L. "Fine Particulate Emissions: Flue Gas Conditioning for Improved Fine Particle Capture in Fabric Filters," Final Technical Report for the Period April 1, 1987, through March 31, 1988; DE-FC21-86MC10637, Grand Forks, ND, August 1988.
9. Laudal, D.L.; Miller, S.J. "Flue Gas Conditioning for Baghouse Performance Improvement with Low-Rank Coals," In *Proceedings of the*

Fourteenth Biennial Lignite Symposium on the Technology and Utilization of Low-Rank Coals; University of North Dakota Energy and Environmental Research Center, Grand Forks, ND, 1987.

10. Miller, S.J.; Laudal, D.L.; Kim, S.S. "Mechanisms of Fabric Filter Performance Improvement with Flue Gas Conditioning," *In Proceedings of the Seventh EPA/EPRI Symposium on the Transfer and Utilization of Particulate Control Technology*; EPRI GS-6208, Vol. 2, February 1989, pp 25-1.
11. Miller, S.J. "Flue Gas Conditioning for Fabric Filter Performance Improvement," Final Project Report for Contract No. DE-AC22-88PC88866 for Pittsburgh Energy Technology Center, December 1989.
12. Miller, S.J.; Laudal, D.L. "Enhancing Baghouse Performance with Conditioning Agents: Basis, Developments, and Economics," *In Proceedings of the Eighth Particulate Control Symposium*; EPRI GS-7050, November 1990, Vol. 2, p 23-1.
13. Miller, S.J.; Laudal, D.L.; Chang, R.L. "Flue Gas Conditioning for Improving Pulse-Jet Baghouse Performance," Presented at the Ninth Particulate Control Symposium, Williamsburg, VA, October 15-18, 1991.
14. Weber, G.F.; Miller, S.J.; Laudal, D.L. "Flue Gas Cleanup," Annual Technical Project Report for the Period July 1, 1989, through June 30, 1990; DE-FC21-86MC10637, Grand Forks, ND, October 1990.
15. Weber, G.F.; Miller, S.J.; Laudal, D.L.; Heidt, M.K. "Flue Gas Cleanup," Semiannual Technical Project Report for the Period January 1, 1991, through June 30, 1991; DE-FC21-86MC10637, Grand Forks, ND, August 1991.
16. Miller, S.J.; Heidt, M.K.; Weber, G.F.; Laudal, D.L. "Flue Gas Cleanup," Semiannual Technical Project Report for the Period July 1, 1991, through December 31, 1991; DE-FC21-86MC10637, Grand Forks, ND, January 1992.
17. Groblicki, P.J.; Wolff, G.T.; Countess, R.J. "Visibility-Reducing Species in the Denver 'Brown Cloud'-- I. Relationships Between Extinction and Chemical Composition," *Atmospheric Environment* 1981, 15, 2473-2484.
18. Watson, J.G.; Chow, J.C.; Pritchett, L.C.; Houck, J.A.; Burns, S.; Ragazzi, R.A. "Composite Source Profiles for Particulate Motor Vehicle Exhaust Source Apportionment in Denver, CO," *In Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 422-436.
19. Trijonis, J.C.; Malm, W.C.; Pitchford, M.; White, W.H.; Charlson, R.; Husar, R. *Visibility: Existing and Historical Conditions--Causes and Effects*; State-of-Science/Technology Report 24, National Acid Precipitation Assessment Program 1990.
20. Hidy, G.M. "Summary of the California Aerosol Characterization Experiment," *Journal of the Air Pollution Control Association* 1975, 25, 1106-1114.

21. Trijonis, J.C. "Visibility in California," *Journal of the Air Pollution Control Association* 1982, 32, 165-169.
22. Conklin, M.H.; Cass, G.R.; Chu, L.C.; Macias, E.S. "Wintertime Carbonaceous Aerosols in Los Angeles," In *Atmospheric Aerosol-Source/Air Quality Relationships*; Macias, E.S. Hopke; P.K. Eds.; ACS Symposium Series 167, Washington, D.C., 1981.
23. Waggoner, A.P.; Weiss, R.E.; Ahlquist, N.C.; Covert, D.S.; Will, S.; Charlson, R.J. "Optical Characteristics of Atmospheric Aerosols," *Atmospheric Environment* 1981, 15, 1891-1909.
24. Covert, D.S.; Waggoner, A.P.; Weiss, R.E.; Ahlquist, N.C.; Charlson, R.J. "Atmospheric Aerosols, Humidity, and Visibility," *Advances in Environmental Science and Technology* 1980, 9, 559-581.
25. Mueller, P.K.; Henry, R.C.; Balson, W.E.; Richards, L.W.; Pitchford, M.; Watson, J.G.; Neff, W.; Saxena, P.; Wilson, W.E. "Future Research on Visibility and Fine Particles: Report from a Panel Discussion," In *Visibility and Fine Particles*; Mathai, C.V. Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 972-989.
26. Porch, W.M.; Charlson, R.J.; Radke, L.F. "Atmospheric Aerosol: Does a Background Level Exist?" *Science* 1970, 170, 315-317.
27. *Air Quality Criteria for Particulate Matter and Sulfur Oxides*, Volume III; EPA-600/8-82-029c, December 1982.
28. Husar, R.B.; Holloway, J.M. "Visibility Trend at Blue Hill, ME, Since 1889," *Bulletin of the American Meteorological Society* 1981.
29. Ferman, M.A.; Wolff, G.T.; Kelly, N.A. "The Nature and Sources of Haze in the Shenandoah Valley/Blue Ridge Mountains Area," *Journal of the Air Pollution Control Association* 1981, 31, 1074-1082.
30. Neff, W.; Watson, J. "Evaluation of the Fuel-Switching Strategy Used in the Denver Brown Cloud Study," In *Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 410-421.
31. Malm, W.C.; Iyer, H.K.; Gebhart, K. "Application of Tracer Mass Balance Regression to WHITEX Data," In *Visibility and Fine Particles*; Mathai, C.V., Ed., TR-17; A&WMA, Pittsburgh, PA, 1990; pp 806-818.
32. Latimer, D.A.; Iyer, H.K.; Malm, W.C. "Application of a Differential Mass Balance Model to Attribute Sulfate Haze in the Southwest," In *Visibility and Fine Particles*; Mathai, C.V., Ed.; TR-17, A&WMA, Pittsburgh, PA, 1990; pp 819-830.
33. Hanson, D. "Haze Obscuring Grand Canyon to be Reduced," *Chemical and Engineering News* 1991, 69, 7.
34. Seinfeld, J.H. *Atmospheric Chemistry and Physics of Air Pollution*; John Wiley & Sons, Inc.: New York, NY, 1986.

35. Novakov, T; Chang, S.G.; Harker, A.B. "Sulfates as Pollution Particulates: Catalytic Formation on Carbon (Soot) Particles," *Science* 1974, 186, 259-261.
36. Latimer, D.A.; Hogo, H. "The Relationship Between SO₂ Emissions and Regional Visibility in the Eastern United States," In Visibility Protection: Research and Policy Aspects; Bhardwaja, P.S., Ed.; TR-10, APCA, Pittsburgh, PA, 1986, pp 589-600.

1. Program/Project Identification No DE-FC21-88MC10637	2. Program/Project Title Flue Gas Cleanup (2.1)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-88
		6. Completion Date 9-30-92

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12. Remarks

Due to the EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date

13. Signature of Recipient and Date
J. Miller 7-31-92

14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Flue Gas Cleanup (2.1)		3. Reporting Period 4-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Fine Particulate Control:				
a.1	Complete reentrainment tests on pore bridging	3-31-92	6-30-92		
a.2	Complete reentrainment tests on dust surface parallel to flow	5-31-92	6-30-92		
Task B	Impact of Coal Combustion on Atmospheric Visibility:				
b.1	Complete literature review on visibility related to coal combustion	1-31-92	6-30-92		
b.2	Define approach to using particle measurement devices to predict atmospheric visibility	5-31-92	6-30-92		
Task C	Final Project Report:				
c.1	Complete Final Project Report	8-31-92			

2.2 Waste Management

WASTE MANAGEMENT

**Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992**

by

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July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

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WASTE MANAGEMENT

1.0 GOALS AND OBJECTIVES

The objective of the Waste Management project at the Energy and Environmental Research Center (EERC) is to characterize waters, waste materials, and by-products from advanced coal preparation and utilization processes, evaluate potential uses for these materials, and identify potentially adverse environmental impacts associated with their use and/or disposal. Research is also being done to develop innovative waste management techniques for conventional and advanced coal utilization processes to comply with existing and/or future environmental regulations.

The goal of the Waste Management project is the understanding and application of:

to all phases of resource management from exploration through development to by-product management.

The activities of the Waste Management project include the following tasks:

- Task 1--Water and Waste Resource Management

Purpose: to investigate the treatability of hot-water-dried (HWD) coal-water fuel (CWF) process water at the bench-scale.

- Task 2--Coal Combustion Ash Conditioning Study

Purpose: to evaluate conditioning procedures for advanced coal utilization wastes.

- Task 3--Bituminous Coal Fly Ash Data Collection and Evaluation

Purpose: to collect and evaluate data concerning the chemical and mineral compositions and physical properties of bituminous coal fly ash.

- Task 4--Waste Depository Scavengers

Purpose: to evaluate inexpensive methods of sorbing and fixing contaminants that have the potential to migrate from coal ash disposal pits.

2.0 ACCOMPLISHMENTS

The following are the accomplishments of the Waste Management project for this reporting period.

2.1 Water and Waste Resource Management

During this reporting period, testing was performed to evaluate the treatability of process water generated from the hot-water drying of Usibelli coal. The process water was treated using two separate bench-scale systems: an activated sludge system and a two-stage, anaerobic, expanded-bed, granular activated carbon system.

Testing was conducted to determine removal rates of selected parameters, such as five-day biological oxygen demand (BOD_5), chemical oxygen demand (COD), and ammonia (NH_3). Results to date from this activity are presented herein.

2.2 Coal Combustion Ash Conditioning Study

The chemical characterization study of the two atmospheric fluidized-bed combustion (AFBC) residues selected for this task was completed. The subtask investigating trace element mobility within conditioned residues was also completed. Leaching characterization of original AFBC residues was completed. Additional subtasks were outlined for potential future research.

2.3 Bituminous Coal Fly Ash Data Collection and Evaluation

Contacts have been made with numerous electric utilities and ash marketing companies in an effort to obtain information and samples of bituminous coal fly ash for this task. As a result of this effort, 57 samples of bituminous coal fly ash from conventional coal combustion power generation facilities were voluntarily submitted for inclusion in this task.

Physical, chemical, and mineralogical characterization of the bituminous coal fly ash samples, as outlined in the work plan, were completed. Additional characterization information was generated on a large number of the samples represented in the database.

The characterization results were placed in a Lotus® 1-2-3® spreadsheet-style database, and the information was also placed into a database manager. Hard copy and disk versions of each of these database formats will be available.

The bituminous coal fly ash database was merged with the existing database of information on low-rank coal fly ash. The complete coal fly ash database now contains information on over 600 samples of coal combustion fly ash from conventional power generation facilities in North America and worldwide.

A similar spreadsheet style database of characterization information on residues from advanced coal processes was also generated utilizing information from previous research projects at the EERC. This database contains information on samples of various materials. Hard copy and disk versions of this database will also be available. A reproducible x-ray powder diffraction

technique for the semiquantitative analysis of advanced coal process residues was developed. This technique utilizes the "Reference Intensity Ratio" method with a zinc oxide (ZnO) internal standard.

2.4 Waste Depository Scavenger Study

The research for this task determined several potentially useful scavenging materials based on attenuation ability, availability, and cost. The scavenging agents targeted for examination included the zeolite mineral clinoptilolite, which is found throughout the western United States in volcanic deposits, bentonite, deposits containing clay minerals, and chars from coal combustion residual material. In laboratory experiments, the clinoptilolite showed the ability to sorb lead and copper from solutions containing high concentrations of these ions.

The initial analytical work indicated that thorough chemical and mineralogical characterization of the individual scavenging materials is necessary. X-ray diffraction (XRD) and x-ray fluorescence (XRF) techniques are useful in determining the initial structure and bulk chemistry of the materials and will provide information on changes that occur during experimentation. Scanning electron microscope/electron probe microanalysis (SEM/EPMA) is also useful in determining the major element composition of the scavenging materials.

3.0 PROJECT RESULTS

3.1 Water and Waste Resource Management

3.1.1 Introduction

The purpose of this task was to assess the characteristics and treatability of the contaminated process water stream derived from the hydrothermal treatment of low-rank coals (LRCs). Coal beneficiation through hydrothermal dewatering has emerged as one of the most promising technologies for upgrading LRCs. Hydrothermal dewatering is a technique used to reduce the water content of high-moisture coals through heating a finely ground coal-water slurry under pressure. The drying temperature is high enough to decompose some carboxyl groups in the coal, forming carbon dioxide. The carbon dioxide then forces the water from the coal pores into the surrounding process water. Reabsorption of water is minimized due to coal surface modification and surface coating with evolved tars and waxes.

Conditions during hydrothermal dewatering, coal chemistry, and coal type have a major impact on the characteristics of coal-water fuel process waters. Many of the contaminants are difficult to remove prior to discharge and may create operational problems if recycled back into the process. Wastewater treatment process selection for coal beneficiation processes is a difficult task. Great emphasis has not been placed on liquid waste management. The need exists for an improved treatability database and a clear methodology for treatment of coal-water fuel waters. Cost-effective production of coal-water fuels can only take place if waste management technologies are developed prior to prototype plant construction. Work on this subtask involves the development of a comprehensive database of process water characteristics and bench-scale testing and evaluation of selected treatment operations.

3.1.2 Research Scope

This task involves bench-scale treatability testing of process water collected during the hot-water drying of coal from the Usibelli coal mine, near Anchorage, Alaska. Based on the information obtained in literature and the chemical and physical characteristics of the contaminated process water, two secondary treatment systems were selected for evaluation, following appropriate preliminary treatment.

3.1.3 Water and Waste Resource Management Study Results

3.1.3.1 Usibelli HWD Process Water Characterization

Modifications to the EERC PDU hot-water drying unit have resulted in two different wastewater streams: condensate and centrate. The condensate stream is generated during the pressure letdown via flash vaporization. The centrate stream is generated during the final centrifugal dewatering step.

Process water used in treatability testing was the centrate stream. A representative sample from the Usibelli HWD CWF process water was collected and submitted to the EERC Analytical Research Laboratory (ARL) for chemical and physical characterization. Table 1 lists the results of characterization analyses of the Usibelli process water.

Approximately 40% of the BOD_5 in the Usibelli centrate can be accounted for in the organic constituents analyzed. Methanol (244 mg/L) contributes the largest percentage to the BOD_5 . The remaining portion of the BOD_5 exists in organic constituents that were not analyzed.

Approximately 80% of the total NH_3 in the centrate exists as free NH_3 and would be steam-strippable. However, pretreatment to reduce the centrate NH_3 was unnecessary since NH_3 levels will not be inhibitory to biological treatment systems at these levels.

The COD: BOD_5 ratio of the centrate stream is approximately 4:1, suggesting that a large portion of the organic matter in the process water is biorefractory, or nonbiodegradable. Therefore, effluent polishing steps will be required under most discharge or reuse situations.

The condensate stream has an even larger portion of biorefractory organics, as indicated by the COD: BOD_5 ratio of approximately 6:1. The organic content of this stream, as measured by COD and phenolics, is nearly three times that of the centrate. A more thorough characterization of the condensate stream is planned. The condensate represents approximately 36% of wastewater flow and has some differentiating physical characteristics, such as the lack of color.

Resource Conservation Recovery Act (RCRA) metals concentrations in the centrate stream are all below maximum contaminant levels.

TABLE 1

Results of Chemical and Physical Characterization Analyses
Performed on Usibelli HWD CWF Process Waters

Parameter/Constituent	Centrate (mg/L)	Condensate (mg/L)
pH	7.2	5.2
Alkalinity	850	---
Ammonia (total)	15	9.5
Ammonia (free)	12	0.28
Chloride	10	---
Fluoride	53	---
Cyanide (total)	0.40	0.32
Nitrate	<1.0	---
Nitrite	<1.0	---
Total Kjeldahl Nitrogen	16	---
Phosphate	3.9	---
Sulfate	6.5	---
Sulfide	---	---
Sulfite	---	---
Thiocyanate	<1.0	---
Thiosulfate	<1.0	---
Total Carbon	1,780	---
Total Inorganic Carbon	640	---
Total Organic Carbon	1,140	930
Chemical Oxygen Demand	3,900	11,300
Biochemical Oxygen Demand	1,000	1,900
Acetate	72	---
Formate	---	---
Propionate	36	---
Butyrate	<5	---
Isobutyrate	28	---
Valerate	18	---
Phenolics (4AAP)	30	184
Phenol+o-Cresol	13	---
p-Cresol	0	---
m-Cresol	5	---
Catechol	0	---
Methanol	244	---
Ethanol	0	---
Acetone	11	---
Propanol	0	---
Methylethylketone	0	---
Propionitrile	0	---

Continued ...

TABLE 1 (continued)
Results of Chemical and Physical Characterization Analyses
Performed on Usibelli HWD CWF Process Waters

Parameter/Constituent	Centrate (mg/L)	Condensate (mg/L)
Total Solids	8670	200
Total Volatile Solids	5580	200
Total Suspended Solids	4930	---
Total Volatile Suspended Solids	3580	---
Total Dissolved Solids	3740	---
Total Volatile Dissolved Solids	2000	200
Conductivity (mmhos)	1.70	0.113
Antimony	<0.05	---
Arsenic	0.18	---
Barium	---	---
Beryllium	<0.05	---
Boron	2.0	---
Cadmium	<0.025	---
Calcium	500	---
Chromium	0.30	---
Cobalt	<0.5	---
Copper	<0.17	---
Iron	38	---
Lead	<0.05	---
Magnesium	100	---
Manganese	0.32	---
Mercury	0.005	---
Molybdenum	---	---
Nickel	0.24	---
Phosphorus	1.3	---
Selenium	<0.05	---
Silver	<0.005	---
Sodium	---	---
Thallium	<0.5	---
Zinc	0.81	---

3.1.3.2 Anaerobic Treatment System Testing

3.1.3.2.1 Introduction

Anaerobic systems have traditionally been used to stabilize organic solids from sewage treatment plants. More recently, these systems have become accepted as a viable means of treating high strength wastewaters (Grady and Lim, 1980).

Anaerobic treatment uses microorganisms that thrive in an environment having a substantial amount of organic matter, in which there is no molecular oxygen. The anaerobes hydrolyze the biodegradable organic matter, producing a variety of simpler compounds such as organic acids, CO₂, and H₂. These compounds are then microbially converted to methane (Grady and Lim, 1980).

The biochemical equation for anaerobic metabolism is:

Combined oxygen includes such sources as NO_3^{-1} , PO_4^{-3} , SO_4^{-2} , and CO_3^{-2} . Gases such as H_2S , H_2 , and N_2 are some of the other end products of anaerobic metabolism (Reynolds, 1982).

The conversion of organic matter to methane involves two groups of anaerobes. The first group, nonmethanogenic bacteria, converts the complex organics into low molecular weight organic compounds, such as organic acids, CO_2 , and H_2 . This group is composed of both fastidious obligate anaerobes and facultative bacteria. The predominant bacterial species in this group are gram-negative, nonspore-forming bacilli (Grady and Lim, 1980).

Methanogenic bacteria make up the second group of anaerobes and are responsible for the production of methane gas. These bacteria are highly substrate specific and depend on the nonmethanogenic bacteria for their supply of substrate. Methanogens are typically obligate anaerobes that tend to be unrelated morphologically, ranging from minute cocci and larger sarcina to individual and chain-forming bacteria. The aspects that these bacteria have in common are that they can only utilize a limited number of substrates (methanol, formic acid, acetic acid, CO_2 , CO , and H_2) and that they produce methane gas (Grady and Lim, 1980).

There are several advantages associated with anaerobic treatment processes. Some of the most important include the production of methane, a valuable end product; lower energy requirements, compared to aerobic processes, because no aeration is required; and relatively low sludge production, as compared to aerobic processes. The anaerobes degrade organic compounds, producing a residual sludge which is inoffensive and which can be used as a soil conditioner and low-grade fertilizer (Grady and Lim, 1980).

There are also some disadvantages associated with these anaerobic processes. Because of the symbiotic nature of anaerobic cultures, they are susceptible to system upsets, thus requiring close supervision and control. After an upset has occurred, these systems are sometimes sluggish at returning to their original condition. Also, because of the requirement for heat exchange, capital costs for anaerobic systems may be high. However, when treating high-strength wastewaters is of importance, the advantages of anaerobic processes generally outweigh the disadvantages (Grady and Lim, 1980).

When anaerobic processes are combined with granular activated carbon, the removal rate of organic contaminants is substantially increased. The granular activated carbon serves several purposes. First, it provides a surface for the attachment of the biofilm. Carbon also serves to remove color and odor from the water. The carbon is also responsible for removing the biorefractory, or nonbiodegradable, compounds. The accumulation of the biorefractory constituents continues until the adsorptive capacity of the carbon is exhausted and a breakthrough occurs (Suidan et al., 1987).

3.1.3.2.2 Anaerobic Treatment System Description and Operation

A schematic of the bench-scale, two-stage, anaerobic, expanded-bed, granular activated carbon treatment system used for the treatability testing of HWD Usibelli wastewater is shown in Figure 1.

The columns were initially seeded with an anaerobic culture obtained from the Moorhead, Minnesota, municipal wastewater treatment facility. Five milliliters of a trace mineral and vitamin solution (Table 2) are added to each liter of influent to supply necessary nutrients for the anaerobic bacteria in the column. The filtered process water is then fed through a peristaltic pump into the columns.

The process water is recycled through the columns to maintain expansion of the carbon bed. The carbon bed is supported by stainless steel mesh screens at the bottom of the columns. Screens are also located at the top of the columns to prevent carbon losses from the system.

Methane gas generated through anaerobic decomposition of organic matter escapes through the top of the columns. The volume of gas produced is then measured by water displacement in the gas collection system.

Column effluent flows from the uppermost port on the side of the column header into a 0.650 L (0.172 gal) covered clarifier. Settled solids are removed periodically from the bottom of the clarifier. Column effluent then overflows a weir into a surge tank maintained under a nitrogen atmosphere. In the two-stage system, the water from the surge tank is then fed as influent into the second column. The surge tank acts as a reservoir, maintaining enough volume of water to feed into the second column in the event of operational problems in the first column.

Each column is encased by a second acrylic cylindrical column with a length of 91.44 cm (36 in) and an inside diameter of 6.35 cm (2.5 in) serving as a water jacket to maintain a constant temperature of 98.5°F (36.9°C), conditions ideal for anaerobic metabolism. Distilled water is pumped from a heated water reservoir, through the jackets surrounding the columns, and back to the reservoir.

Table 3 lists the physical parameters and the operating conditions of the fully operational bench-scale, two-stage, anaerobic, expanded-bed, granular activated carbon treatment system. Currently, Columns 2 and 3 are operating in series while Column 1 is operating independently.

Initially, 0.454 kg (1 lb) of granular activated carbon was added to each column. However, due to early operational problems, some carbon was lost in Columns 1 and 2, which accounts for the difference in the mass of adsorbent in Table 3.

Table 4 lists the maintenance performed on the two-stage, anaerobic, expanded-bed, granular activated carbon treatment system. Daily measurements are taken of influent and effluent tank levels, influent and effluent pH, gas production, expanded bed height, water reservoir temperature, nitrogen cylinder pressure, and nitrogen purge flow rate. Influent rates are measured and adjusted daily.

Figure 1. Two-stage, anaerobic, expanded-bed, granular activated carbon treatment system schematic.

TABLE 2
Chemical Composition of the Nutrient Solution

Chemical	Quantity
Nutrient Solution (1 L)	
Aluminum Sulfate Hydrate	0.01 g
Boric Acid	0.01 g
Calcium Chloride	0.10 g
Calcium Sulfate Dihydrate	0.01 g
Cobalt Chloride Hexahydrate	0.11 g
Iron Sulfate Heptahydrate	0.10 g
Magnesium Sulfate Heptahydrate	3.00 g
Manganese Sulfate Hydrate	0.50 g
Nitriloacetic Acid	1.50 g
Potassium Molybdate Dihydrate	0.01 g
Sodium Chloride	1.00 g
Zinc Sulfate Heptahydrate	0.10 g
Vitamin Solution (100 mL solution)*	
p-Aminobenzoic Acid	10.0 mg
Biotin	4.0 mg
Folic Acid	4.0 mg
Nicotinic Acid	10.0 mg
Pantothenic Acid	10.0 mg
Pyridoxine Hydrochloride	20.0 mg
Riboflavin	1.0 mg
Thiamine Hydrochloride	10.0 mg
Thioctic Acid	10.0 mg
Vitamin B ₁₂	0.2 mg

* 0.5-mL vitamin solution is added to 1 L of nutrient solution.

TABLE 3

Physical Parameters and Operating Conditions for the Two-Stage,
Anaerobic, Expanded-Bed, Granular Activated Carbon Treatment System

Parameter		Quantity
Column		
Length		91.44 cm (36 in)
Inside Diameter		5.08 cm (2 in)
Outside Diameter		5.72 cm (2.25 in)
Influent/Effluent Header		
Length		10.16 cm (4 in)
Inside Diameter		5.08 cm (2 in)
Outside Diameter		5.72 cm (2.25 in)
Water Jacket		
Length		91.44 cm (36 in)
Inside Diameter		8.89 cm (3.5 in)
Outside Diameter		10.16 cm (4 in)
Influent Feed Rate		
Usibelli Wastewater		1 L/day (0.264 gal/day)
Nutrient Solution		5 mL/day (0.0013 gal/day)
Design Column Recycle Rate		0.660 L/min (0.174 gal/min)
Adsorbent*		
Column 1		0.397 kg (0.875 lb)
Column 2		0.404 kg (0.891 lb)
Column 3		0.454 kg (1.000 lb)
Bed Height		
Column 1	Static	49.3 cm (19.4 in)
	Expanded	53.2 cm (20.9 in)
Column 2	Static	50.2 cm (19.8 in)
	Expanded	54.5 cm (21.5 in)
Column 3	Static	56.4 cm (22.2 in)
	Expanded	63.5 cm (25.0 in)
System Temperature		36.9°C (98.5°F)

* Adsorbent: Calgon F-400 granular activated carbon (16 x 20 mesh).

TABLE 4

Routine Anaerobic System Maintenance Performed
During Usibelli Process Water Treatability Study

Control Parameter	Frequency
Measure influent tank levels	Daily
Measure effluent tank levels	Daily
Measure pH of influent and effluents	Daily
Measure expanded bed heights	Daily
Measure gas production	Daily
Measure water reservoir temperature	Daily
Measure nitrogen cylinder pressure	Daily
Measure nitrogen purge flow	Daily
Measure and adjust feed rate	Daily
Replace feed tubing	1/week
Replace recycle tubing	2/week
Measure COD of influent and effluents	2/week
Measure color	2/month
Measure gas composition	1/month

Feed tubing is replaced once a week, while the recycle tubing is replaced once every four days. Color is measured once every two weeks, and gas composition is measured once a month.

Table 5 provides a chronological summary, to date, for the anaerobic treatment system, describing significant events during treatment system operation.

The anaerobic treatment system began operation on 12/10/91 (Day 1) with the start-up of Column 1. Prior to operation, each column was hydrostatically tested by filling both the inner cylinder and outer water jacket with distilled water and allowing it to set for a 24-hour period. One pound (0.454 kg) of granular activated carbon was then added to the column. The column was then seeded with approximately 20 mL of an acclimated anaerobic culture.

Prior to secondary treatment, the process water was filtered through 0.45- μ m hydrophilic, polysulfone membrane, high-capacity filters to remove coal particles. Filtering was required because of the high total suspended solids (TSS) in the centrate stream. This pretreatment step is intended to simulate conditions of CWF recovery at an actual operating facility.

Filtered process water was initially fed into Column 1 at 100-mL intervals, increasing by 100 mL every two days, until a rate of 1 L/day (0.264 gal/day) was achieved (Day 38). Gas production was observed on Day 28 of operation. The process water was recycled through the column at a nominal rate of 0.660 L/min (0.174 gal/min). This rate was established to maintain bed expansion, allowing gas bubbles to migrate as discrete particles to the top of the column. Column 1 effluent drained from the column into a clarifier where the solids were gravity-separated from the water. Clarifier effluent

TABLE 5

Chronological Summary of Two-Stage, Anaerobic, Expanded-Bed,
Granular Activated Carbon Treatment System

Date	Day of Operation	Comments
12/10/91	1	Began system operation. Seeded Column 1. Began feeding 100-mL influent daily.
01/01/92	22	Increased influent rate to 200 mL/d.
01/03/92	24	Increased influent rate to 300 mL/d.
01/05/92	26	Increased influent rate to 400 mL/d.
01/07/92	28	Increased influent rate to 500 mL/d. Noted methane production in Column 1. Observed biomass floating above carbon bed.
01/09/92	30	Increased influent rate to 600 mL/d.
01/11/92	32	Increased influent rate to 700 mL/d.
01/13/92	34	Increased influent rate to 800 mL/d.
01/15/92	36	Increased influent rate to 900 mL/d.
01/17/92	38	Increased influent rate to 1000 mL/d.
01/22/92	43	Column 2 placed in series with Column 1. Added 454-g granular activated carbon. Did not seed Column 2 with microbes. Influent rate to Column 2 at 1 L/d of Column 1 effluent.
01/25/92	46	Water recycle pump stopped. Column 1 methane production ceased during this "cold" condition. Worn brushes were replaced in pump. Gas production was observed again as soon as the pump was fixed and recycling warm water.
01/31/92	52	Began routine COD sampling and analyses.
02/14/92	66	Began routine gas sampling and analyses.
02/21/92	73	Began periodic color analyses on influent and Column 1 and 2 effluents.

Continued ...

TABLE 5 (continued)

Chronological Summary of Two-Stage, Anaerobic, Expanded-Bed,
Granular Activated Carbon Treatment System

Date	Day of Operation	Comments
03/10/92	91	Increased COD analyses to twice a week.
04/12/92	124	Influent rate to Column 1 was set too high. The feed container was empty, and air was inadvertently introduced into the column. No adverse effects were observed.
04/22/92	134	Inadvertently added 550-mL influent to surge tank.
04/26/92	138	Column 1 feed container empty. Air was fed into Column 1. Again, no adverse effects were noted. Decreased feed set point to Column 1.
05/11/92	153	Observed gas bubbles in Column 2 as a result of Day 134.
05/19/92	161	Air introduced to both columns. Both Column 1 influent tank and surge tank to Column 2 were empty.
05/21/92	163	Noted disappearance of gas bubbles from Column 1.
05/24/92	166	Gas production in Column 1 reappeared.
05/26/92	168	Air was fed into Column 1 as a result of feed tube halfway out of influent container. No effect on gas production observed. Column 3 prepared for on-line installation.
05/28/92	170	Observed significant gas bubbles in Column 2. This gas production continued. Changed system configuration by replacing Column 1 with Column 3. Column 2 now lead column. Column 1 operating independently.

Continued ...

TABLE 5 (continued)

Chronological Summary of Two-Stage, Anaerobic, Expanded-Bed,
Granular Activated Carbon Treatment System

Date	Day of Operation	Comments
05/29/92	171	Water jacket leaked, resulting in system heat loss. All columns at room temperature. Gas production observed in Column 1, but not in Column 2. Took Column 3 off-line.
05/30/92	172	Gas production observed in Column 2.
05/31/92	173	Began feeding Column 3 even though the water jacket was not repaired. Noticed heat losses in the system by measuring water jacket temperatures at various locations.
06/12/92	185	Column 1 water jacket began leaking. Column 3 water jacket continues to leak. Drained water from both water jackets and attempted to repair them.
06/15/92	188	Column 3 water jacket repaired.
06/16/92	189	Column 3 fully operational. Column 1 water jacket repaired.
06/17/92	190	Column 1 water jacket fully operational. Observed gas bubbles in Column 3.

overflowed a centrally located weir and was collected in the surge tank. The surge tank allowed sufficient capacity for a two-day supply of water to subsequent columns. A nitrogen-purge was added to the surge tank to prevent air from entering the container.

Column 2 was placed in series with Column 1 on Day 43. Effluent from Column 1, draining into the surge tank, was used as the influent to Column 2. Column 2 was operated under the same conditions as Column 1. Methane production was observed in Column 2 on Day 140.

Columns 1 and 2 were operated in series for 127 days, until Column 1 reached carbon exhaustion, as measured by effluent COD. Column 1 was removed from the two-stage system and is currently being operated independently to observe potential inhibitory effects of biorefractory organics.

Filtered process water is currently being fed directly to Column 2, the lead column, at a nominal influent rate of approximately 1 L/d. The effluent from Column 2 is being collected in the surge tank, of which the contents are being fed into Column 3. Gas production was observed in Column 3 on Day 190. Presently, all three columns are exhibiting gas production.

One of the operational problems encountered with this system included recycle tubing wear and subsequent leaking. To avoid this problem, the recycle tubing is changed once every four days. Another problem encountered was running out of feed and pumping air into the system because the influent rate was set too high. This difficulty is prevented by daily monitoring of the influent rate and adjusting the feed set point as necessary.

One of the more common operational monitoring difficulties with the system was the loss of gas through the effluent line because of pressure differences. It is difficult to measure the gas production accurately when a portion of the gas escapes through the effluent. A daily attempt is made to equalize the pressure in the system so that the gas will flow to the collection system and not be lost through other streams.

Perhaps the most serious problem that has been encountered involved leaking water jackets. Although the jackets were repaired and fully operational within two weeks, the change in temperature from 98.5°F to approximately 70°F may have had a negative effect on the microbial environment, resulting in a decrease of effluent quality.

3.1.3.2.3 Anaerobic Treatment System Results

CHEMICAL OXYGEN DEMAND (COD)

Figures 2 through 4 illustrate the relationship between COD and the system throughput volume. Figure 2 shows Column 1 influent and effluent COD as a function of throughput volume. Breakthrough (400-mg/L COD) occurred at approximately 34 L of throughput, corresponding to 34 bed volumes. Carbon exhaustion was estimated to occur after approximately 150 L of throughput, or 150 bed volumes. Exhaustion was assumed to occur at a column effluent COD of 3200 mg/L, or 1200 mg/L less than the influent COD. The 1200 mg/L difference represents the biodegradable fraction of COD, as measured by BOD₅.

Column 1 was taken off-line after 150-L throughput (carbon exhaustion) and was continued in independent operation to observe any potential microbial inhibition following carbon exhaustion. Effluent COD levels appear to be slowly increasing, without corresponding increases in influent COD, indicating incomplete biodegradation of organics, as measured by BOD₅. Column 1 gas generation rates were also observed to decrease over this same operating period. However, independent operation of Column 1 resulted in operation at a temperature of 6 to 7 degrees lower than the design temperature of 98.5°F, due to necessary placement of the column with respect to the location of the heat exchange reservoir. Reduced operating temperatures are believed to be the reason for reduced anaerobic activity, rather than microbial inhibition. System design modifications will allow for the maintenance of constant temperature across all three operating columns. Subsequent testing is also planned to further evaluate the effects of temperature variations on anaerobic degradation of Usibelli HWD process water.

Figure 2. Chemical oxygen demand vs. throughput: Column 1.

Figure 3. Chemical oxygen demand vs. throughput: Column 2.

Figure 4. Chemical oxygen demand vs. throughput: overall system.

Figure 3 is a plot of Column 2 COD as a function of throughput. At approximately 125 L of throughput, (Day 169), the system configuration was changed. Column 2 became the lead column for two-stage system operation ahead of Column 3. Prior to Day 169 of operation, influent to Column 2 consisted of Column 1 effluent. After that time, Column 2 was fed filtered Usibelli HWD process water. This change is indicated by a significant increase in system influent COD levels. Operation of two columns in series significantly extended the time to effluent COD breakthrough. This increased utilization of adsorption capacity approximately tripled the throughput to breakthrough while roughly only doubling the amount of carbon. Two-stage operation will also allow for complete exhaustion of the column prior to being taken off-line. Overall system operation is illustrated in Figure 4. Limited data for Column 3 were available at the time of preparation of this report.

COLOR

One of the parameters used to evaluate system performance of the anaerobic treatment system was color. The color of the process water was measured visually using a Hach color comparator, which involves comparing the color of the sample with calibrated plastic color disks. Because turbidity can cause the apparent color determinations to be significantly greater than those of true color, all samples were filtered prior to measurement (American Public Health Association, 1985).

The color value of the HWD process water is extremely pH-dependent, increasing as the pH of the water increases. Because the pH of the process water remained relatively constant throughout the measuring period, the increase in effluent color can only be attributed to carbon exhaustion.

Table 6 lists the average influent and effluent color for the three columns. Color units are reported as platinum-cobalt (Pt-Co) units. The bed volumes (L) at each day of operation are provided in parentheses following the values listed for color.

GAS ANALYSIS

Gas composition was measured approximately once a month. Table 7 shows the composition of the gas generated from Column 1 as well as a few physical and thermal properties. The heating value of the gas is of particular importance since the production of methane is one of the advantages of using anaerobic treatment systems.

Overall, twenty of the more common gases are scanned for during the analysis. Of these twenty gases, only five were present in all of the analyses conducted on the gas generated by Column 1, including hydrogen (H_2), carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), and methane (CH_4). Future analyses will include the gas generated by Columns 2 and 3.

As observed in Table 7, the ratio of oxygen to nitrogen (20:80) indicates that air was introduced into the method of gas sampling. If air had not been present, the mole percent of methane would be well over 90%. One of the possible, and most likely, pathways in which air was introduced is during the gas sampling procedure. Air may have entered the gas sampling bag during the transfer of gas from the collection system to the bag, or the gas sampling bag itself may allow some air to permeate it, or the seal around the port may not have been tight. To determine the source of error, a different gas collection bag will be used. If this is not the source of error, a new method of gas sampling will be devised.

TABLE 6

Results of Color Analyses for the Two-Stage, Anaerobic, Expanded-Bed, Granular Activated Carbon Treatment System

Average Influent Color: 25,000 Pt-Co Units			
Day of Operation	Color		
	Column 1 Effluent	Column 2 Effluent	Column 3 Effluent
80	1200 (53 L)	50 (35 L)	
90	3500 (65 L)	250 (46 L)	
100	20000 (75 L)	200 (60 L)	
150	20000 (131 L)	1000 (109 L)	
170	20000 (146 L)	2500 (123 L)	
190	25000 (172 L)	12500 (148 L)	150 (21 L)

TABLE 7
Column 1 Gas Composition

Day of Operation:	66	99	120	147	196
Component (mole percent)					
Hydrogen	0.05	0.08	0.05	0.05	0.05
Carbon Dioxide	1.25	1.90	2.20	2.66	1.06
Oxygen/Argon	5.38	2.90	6.16	5.18	7.92
Nitrogen	24.61	13.40	26.04	21.95	36.86
Methane	68.71	81.73	65.55	70.16	54.11
Heating Value (Btu/scf)					
Saturated	684.4	814.3	652.8	698.8	538.8
Dry	696.5	828.7	664.3	711.2	548.3
Specific Gravity	0.698	0.644	0.717	0.699	0.760
Average Molecular Weight	20.19	18.63	20.75	20.23	22.01

Figure 5 presents the cumulative volume of gas generated by each column. Gas production in Column 1 was observed as early as Day 28 of operation. However, a measurable quantity of gas was not produced until Day 55. The gas production remained relatively constant, with a few exceptions. For example, because of difficulties in equalizing the pressure, some gas was lost through the effluent discharge line. This is illustrated by a decrease in slope between Days 80 and 90 of operation. Once this situation was corrected, the slope continued to increase consistently until the system configuration was changed. On Day 185, approximately two weeks after Column 1 was removed from two-stage operation and placed into independent operation, the water jacket leaked, exposing the column to room temperatures for about one week. This reduced temperature resulted in a decreased gas production rate which is represented by a decrease in the slope corresponding to Column 1.

Column 2 was placed into operation on Day 43. However, gas production was not observed until Day 172 of system operation. The lag period for gas generation from Column 2 can be attributed to Column 1 effluent being fed to the system. When biodegradable organics were introduced to Column 2, gas generation developed rapidly. The volume of methane produced is directly related to the influent COD (Suidan et al., 1987). On Day 134, untreated process water was inadvertently added to the surge tank. Within a week, gas production was observed in Column 2, continued for approximately three days, and then disappeared. On Day 153, gas was once again observed in the column, but was not generated in sufficient volumes for collection until Day 170, as illustrated in Figure 5.

Figure 5. Cumulative gas generated vs. time: overall system.

Figure 6 illustrates the relationship between the COD loading and the gas generated in Column 1. The regression line is represented by the equation: $y = 0.156x + 0.039$. Thus for each 100 grams of COD applied to the system, approximately 16 L of gas are generated. Grady and Lim (1980) have reported theoretical methane generation rate at 16 grams of methane produced for every 64 grams of COD removed from wastewater.

3.1.3.3 Aerobic Treatment System

3.1.3.3.1 Introduction

An activated sludge process was selected for the evaluation of an aerobic system for the treatment of Usibelli HWD process water. Biomass used to seed the reactor was obtained from an activated sludge system operating on mild gasification process condensates.

The activated sludge process utilizes a suspended, mixed growth of aerobic microorganisms that use the organic materials in wastewaters as substrates. These substrates are removed through microbial respiration and synthesis of new cells.

The biochemical equation for the activated sludge process is:

Other end products include NH_4^{+1} , NO_2^{-1} , NO_3^{-1} , and PO_4^{-3} .

Figure 6. Cumulative gas generated vs. cumulative COD applied: Column 1.

Aerobic organisms can generally be divided into four nondistinct classes including floc-forming organisms, saprophytes, predators, and nuisance organisms. The floc-forming organisms are responsible for gravity settling and removal of the sludge from the treated wastewater. Saprophytes are responsible for degrading the organic matter. This class of bacteria is composed mostly of gram-negative bacilli. Approximately 230 species of predators, usually protozoa which feed on the bacteria, have been reported to occur in activated sludge. Nuisance organisms are usually filamentous bacteria and fungi which inhibit sludge settling (Grady and Lim, 1980).

A mean cell residence time (MCRT), also called sludge age, is used to determine the average time a microbial cell remains in the system. The MCRT, along with the food-to-microorganism ratio (F/M), are used to characterize the efficacy of an activated sludge process. A high F/M coupled with a low MCRT indicate the presence of filamentous growths, nuisance organisms, which create poor settling conditions. A low F/M and a high MCRT generally cause biological solids to undergo degradation and cell dispersion (Reynolds, 1982).

3.1.3.3.2 System Description and Operation

A schematic of the bench-scale activated sludge system used for treatability testing of Usibelli HWD process water is shown in Figure 7. The activated sludge aeration tank consists of a 10-L plexiglass basin with an operating volume of 6 to 8 L. Mixed liquor is maintained in suspension with a mechanical mixer. Oxygen is metered to the system as filtered, humidified, compressed house air through coarse-bubble diffusers.

Figure 7. Bench-scale activated sludge treatment system schematic.

Essential nutrients for the growth of microorganisms are nitrogen and phosphorous. Coal-processing wastewaters are typically deficient in phosphorus. However, testing of the HWD Usibelli process water showed it to be deficient in both nutrients. Nitrogen and phosphorus, in the form of ammonium hypophosphate ($[\text{NH}_4]_2\text{HPO}_4$), were added to the influent to obtain a $\text{BOD}_5\text{:N:P}$ ratio of 100:5:1.

The MCRT was controlled by volumetric wasting of mixed liquor measured in conjunction with the mass of mixed liquor volatile suspended solids (MLVSS) in the reactor and the concentration of volatile suspended solids lost in the effluent each day. The hydraulic retention time (HRT) was controlled through regulation of the influent rate in relation to the aeration basin volume.

Daily measurements were taken of the influent rate, influent pH, mixed liquor pH, and mixed liquor dissolved oxygen, with adjustments being made as necessary. Settleable solids and dissolved oxygen uptake rate readings were taken on every sampling day. Routine maintenance procedures are listed in Table 8.

Routine analyses were performed once a week on the system. Analyses include measurement of TSS, volatile suspended solids (VSS), COD, BOD_5 , and NH_3 .

Filtered process water was fed from a 2-L graduated cylinder to the aeration basin with a peristaltic pump. Initially, the system was operated using a continuous-flow configuration whereby mixed liquor flowed by gravity

TABLE 8

Routine Activated Sludge System Maintenance Performed
During Usibelli Process Water Treatability Study

Control Parameter	Frequency
Measure volume in feed tank	Daily
Measure volume in effluent tank	Daily
Measure pH of feed and mixed liquor	Daily
Measure mixed liquor temperature	Daily
Measure mixed liquor dissolved oxygen	Daily
Clean aeration basin and clarifier walls	Daily
Measure dissolved oxygen uptake rate	Variable
Measure mixed liquor settleable solids	Variable
Measure and adjust feed rate	1/week
Replace feed and recycle tubing	1/week
Waste mixed liquor from aeration basin	Variable
Recalibrate pH meter	1/week
Change dissolved oxygen probe membrane	Periodically

to a secondary clarifier with an operating volume of approximately 650 mL. Biological solids settled to the bottom and were recycled to the aeration basin every 20 minutes. Treated effluent and nonsettleable solids overflowed a centrally located weir and were collected in a 6-L effluent storage container.

Table 9 provides a chronological summary, to date, of the activated sludge treatment process. It describes significant events concerning the treatment system.

With this continuous-flow configuration, BOD₅ effluent values were erratic and relatively high. Nutrient addition to the system was increased to assure that these high effluent BOD₅ values were not a result of nitrogen and/or phosphorus deficiency. Additionally, erratic and high losses of VSS to the effluent was occurring. In order to maintain a stable population of microorganisms and allow for better process control, system operation was converted to a fill-and-draw configuration.

Two liters of filtered process water were fed over a 24-hour period into the aeration basin. The mixed liquor volume fluctuated between 6 and 8 L. At the end of the 24-hour period, the contents of the aeration basin were allowed to settle, undisturbed, for 30 minutes. Two liters of supernatant was then withdrawn from the system. This method served to increase the MLVSS and subsequently reduce effluent BOD₅. Results, to date, have shown a significant reduction in effluent BOD₅ values.

Another problem, contributing to poor treatment, observed with the activated sludge system was excessive foaming in the reactor. Foaming is now controlled by adding approximately 2 mL of dilute antifoam, a silicon-based polymer, directly to the reactor. This antifoam is beneficial because it

TABLE 9
Chronological Summary of the Activated Sludge System

Date	Day of Operation	Comments
11/26/91	1	Began activated sludge operation. Seeded reactor with sludge from an activated sludge system treating mild gasification wastewater.
12/10/91	15	Began routine measurement of solids settleability and dissolved oxygen uptake.
12/26/91	31	Excessive foaming observed in reactor.
12/27/91	32	Began adding antifoam to reactor.
01/04/92	40	pH-adjusted mixed liquor from 7.6 to 6.8.
01/07/92	43	Began adding antifoam to influent tank.
01/13/92	49	Began routine analyses for BOD ₅ , COD, NH ₃ , and suspended solids.
02/04/92	71	Began adding antifoam directly to reactor.
02/25/92	92	Reduced the frequency and sampling analysis.
03/26/92	122	Began wasting 80 mL/d of mixed liquor.
04/10/92	137	Increased nutrient volume from 1 mL nutrient/L water to 2 mL nutrient/L.
04/16/92	143	Reduced the frequency and sampling analysis.
06/02/92	190	Changed system configuration from continuous to fill-and-draw mode. Discontinued wasting 80 mL/d of mixed liquor.

effectively controls foaming without depleting the oxygen in the mixed liquor, as is common with most antifoaming agents.

3.1.3.3.3 Treatment System Results

Figure 8 shows the relationship between mixed liquor and effluent suspended solids as a function of time. With continued operation, the ratio of MLVSS/mixed liquor suspended solids (MLSS) appears to decrease, indicating a higher fraction of nonvolatile solids. Solids data from operation between days 50 to 100 showed that approximately 50% of the MLSS was MLVSS. Data collected just prior to Day 200 indicate that the MLVSS/MLSS ratio has decreased to approximately 40%.

Figure 9 is a plot of MCRT during the 30-week operating period. The erratic nature of the MCRT can be directly attributed to fluctuations in effluent suspended solids (effluent total suspended solids [ETSS] and effluent volatile suspended solids [EVSS]).

BOD₅ removals of 95% were achieved during activated sludge treatment of Usibelli process water. The average BOD₅ concentration in the influent, 1220 mg/L, was reduced to as low as 31 mg/L, but was not consistent. The treatability target discharge goal for BOD₅, based on New Source Performance Standard (NSPS), was 30 mg/L.

The average influent total COD during the operating period was 4540 mg/L. Average effluent soluble COD was 3730 mg/L, an 18% removal rate. Figure 10 illustrates influent and effluent COD as a function of time. This concentration is much higher than the target NSPS effluent quality goal of 400 mg/L. High concentrations of refractory COD in the activated sludge effluent will require further treatment.

Figure 8. Suspended solids vs. time.

Figure 9. Mean cell residence time vs. time.

Figure 10. Chemical oxygen demand vs. time.

Figure 11 shows influent and effluent ammonia. Average influent ammonia was 13 mg/L. Effluent ammonia averaged 2 mg/L, resulting in a removal efficiency of 83%. Ammonia removals during activated sludge treatment are most likely the result of air stripping in the aeration basin, rather than biological nitrification. No increase in effluent nitrate was detected.

Table 10 summarizes operating parameters for the activated sludge system during this phase of operation.

Figure 11. Ammonia vs. time.

TABLE 10

Summary of Operating Parameters
Activated Sludge Treatment of Usibelli HWD Process Water

Hydraulic Retention Time (HRT)	3.3 d
Mean Cell Residence Time (MCRT)	20 d
Food-to-Microorganism Ratio (F/M)	0.0034 g BOD ₅ /g MLVSS/d
Mixed Liquor Volatile Suspended Solids (MLVSS)	1630 mg/L
Oxygen Uptake Rate	0.112 mg/L/min 141.8 mg/g/hr

3.2 Coal Combustion Ash Conditioning Study

3.2.1 Introduction

Atmospheric fluidized-bed combustion (AFBC) is an advanced coal combustion technology used to control SO_2 emissions. In addition, this process produces lower levels of nitrogen oxides than conventional pulverized coal (PC) units because of lower operating temperatures. Because of SO_2 and NO_x removal during the combustion process, physical and chemical properties of wastes generated differ from those of PC units. Consequently, traditional waste management systems used for PC units may be inappropriate to efficiently condition and dispose of AFBC wastes (Golden, 1988).

This report presents a conceptual design for an innovative ash conditioning system to handle a "self-heating" mixture of 65% char and 35% fly ash produced by an existing AFBC facility. The design is based on the physical and chemical behavior of the ash. Critical waste properties tested include heat of hydration, compressive strength, time of set, rate of hydration, viscosity, bulk and packed density, and gradation.

3.2.1.1 Atmospheric Fluidized-Bed Combustion Process

Atmospheric fluidized-bed combustion (AFBC) is a relatively new technology which may reduce SO_2 emissions associated with acid rain problems currently concerning regulators and the public. There are two basic types of AFBC processes, a bubbling bed and a circulating bed. They are similar in that they both use cyclones to recycle solids back to the fluidized bed. But they differ with regard to fluidization air velocity, combustion particle size, and location of the heat-transfer surface for steam generation. The bubbling-bed process operates at a 4- to 12-ft/sec superficial (air) gas velocity and 0.5- and 0.1-inch coal and limestone particle sizes, respectively. The heat-transfer surface is located both in the fluidized bed and in the convective pass ahead of the cyclone. The circulating-bed process operates with a 15 to 25 ft/sec superficial gas velocity and 0.2- and 0.04-inch coal and limestone particles, respectively. Heat-transfer surfaces are located either at the top of the furnace or as an external heat exchanger. Both processes produce a char stream which is taken from the cyclone system (Golden, 1988; RP 2708-1, 1988).

The AFBC process offers two main advantages over conventional PC technologies: fuel flexibility and high SO_2 removal levels (90%-95%) without postcombustion controls. To achieve the high SO_2 removal level associated with AFBC (a greater than stoichiometric quantity), excess limestone is required to react in the combustion bed. Therefore, a larger quantity of dry solid waste is produced than that of conventional coal-burning technologies. As an example, the removal of 1 kg of sulfur produces approximately 6 kg of spent sorbent at a Ca:S ratio of 2:3. AFBC wastes differ from PC wastes because of the lower combustion temperatures and large limestone addition rates (Golden, 1988; RP 2708-1, 1988; Smith, 1989).

There are three basic AFBC solid waste streams produced during combustion (RP 2708-1, 1988):

- Spent Bed Material (SBM)--waste withdrawn from the bottom of the boiler

- AFBC fly ash--flue gas residue collected by either a fabric filter baghouse or an electrostatic precipitator
- Char--coarser flue gas residue collected by a primary particulate device, typically a cyclone

During the combustion process, crushed coal and limestone of the appropriate particle size are fed into the combustion chamber. A distributor plate distributes a high-velocity air stream throughout the combustion chamber to fluidize the bed. As the coal ignites, it reacts with the limestone which in turn absorbs/ reacts with the sulfur contained in the coal.

The combustion heats water running through boiler tubes to produce steam for electric power generation. As the coal burns, flue gas containing fine-solid particles leaves the combustion chamber. A primary dust collection system, usually a multitube cyclone, removes larger particles or char in the 1- μm and larger range. Fine dust particles or fly ash in the 0.001- to 1.0- μm range are removed from the escaping flue gas with either a baghouse or an electrostatic precipitator (Wark and Warner, 1981).

3.2.1.2 AFBC Ash Description

An important characteristic of the AFBC ash for both disposal and utilization is its exothermic behavior upon water addition. Available information indicates that the water added during conditioning reacts with calcium and magnesium oxides and, to a lesser extent, with calcium sulfate in the waste (Golden, 1988). These hydration reactions occur as follows (RP 2708-1, 1988):

1. $\text{CaO}_{(s)} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_{2(s)} + \text{heat}$
2. $\text{MgO}_{(s)} + \text{H}_2\text{O} \longrightarrow \text{Mg(OH)}_{2(s)} + \text{heat}$
3. $\text{CaSO}_{4(s)} + 2\text{H}_2\text{O} \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}_{(s)} + \text{heat}$

The extent to which these reactions will occur, and thus the amount of heat released, depends on plant operating conditions (variations in feedstock, process temperature, etc.) and the AFBC boiler configuration (RP 2708-1, 1988; Smith, 1989; Wark and Warner, 1981; Bland et al., 1989).

A self-heating ash presents various handling problems that are not associated with conventional PC ashes. For example, the heat produced and released during hydration can cause serious problems for ash-handling equipment components such as bearings, bushings, electric connections and motors, and tires. In addition, the steam released creates a nuisance at the conditioning, transport, and disposal areas. Self-heating ashes also tend to dry out during hydration, stiffen, and set up, making conditioning and transport more difficult (Bazzel and Mallory, 1987).

3.2.2 Objective and Scope

In this task, an innovative conditioning process, that was developed for a self-heating AFBC waste, will be described. This conditioning process involves mixing the waste with enough water to satisfy all of the hydration reactions, to allow for moisture losses due to steam release, and to still

have enough residual moisture content to produce the maximum compacted density when the waste is placed at the disposal site.

The key objectives of the proposed conditioning system were to 1) mix enough water with the ash to produce the optimum moisture content for maximum compacted density in the fully hydrated material, 2) handle the changing consistency of the ash as it hydrates, 3) promote full hydration of the ash under controlled conditions, and 4) provide short-term storage for the hydrated ash until it can be transported to the landfill for ultimate disposal.

Chemical and mineralogical investigations of the original AFBC residues and samples of conditioned AFBC residues will be included in this study to determine the chemical reactions and mineralogical-phase transformations that may occur during the conditioning process. Major, minor, and trace inorganic constituents of the original and conditioned residues will be studied, and experiments will be designed to investigate the mobility of trace inorganic constituents in the conditioned residues.

3.2.3 Coal Combustion Ash Conditioning Study Results

3.2.3.1 Bulk Chemical and Mineralogical Characterization

Chemical characterization of the AFBC residues was completed, and results of the various analyses are included in Table 11. In this study, proton-induced x-ray emission (PIXE) results (included in the last semiannual report) were used to determine an initial list of trace elements for quantitation in the two residues. That list included all Resource Conservation and Recovery Act (RCRA) elements, even if they were not identified by the PIXE results. Other highly mobile elements were also included for completeness. These trace elements are listed in Table 12.

The chemical characterization protocol included the quantitative analysis of the trace elements listed in Table 12 and the major and minor inorganic constituents. Major/minor inorganic constituents, present in percentage amounts in the samples, were silicon, aluminum, iron, calcium, magnesium, sodium, potassium, titanium, phosphorous, strontium, and manganese. Moisture content, loss on ignition, and carbonate were also determined in the original materials. Complete sets of the chemical characterization results (major, minor, and trace element constituents) are included in Table 11.

Mineralogical characterization by x-ray diffraction of the bulk samples was completed. Results are summarized in Table 13.

3.2.3.2 Results of Trace Element Mobility Investigations

These tasks involved the investigation of trace element mobility in test cylinders of the residues conditioned with different levels of moisture and at four curing times. Slices of these conditioned materials were submitted for the trace element mobility investigations. The various conditioned samples received for these investigations are summarized in Table 14, and Figure 12 indicates the area of the cylinder that was selected and submitted. Two slices, approximately 1 inch thick, were taken from the center of each cylinder. One slice was kept intact for the trace element mobility study,

TABLE 11
Bulk Chemical Characterization Results
Black Dog 1 TVA/Shawnee

Moisture:	%	0.47	0.11
Loss on Ignition:	%	27.9	9.25
SO ₃	% Oxide	17.2	16.6
SiO ₂	% Oxide	10.7	10.4
Al ₂ O ₃	% Oxide	4.05	3.55
Fe ₂ O ₃	% Oxide	1.97	4.53
CaO	% Oxide	31.2	49.5
MgO	% Oxide	1.98	2.52
Na ₂ O	% Oxide	0.50	0.07
K ₂ O	% Oxide	0.20	0.42
P ₂ O ₅	% Oxide	0.24	0.05
TiO ₂	% Oxide	0.23	0.05
BaO	% Oxide	0.20	0.03
MnO ₂	% Oxide	0.02	0.02
SrO	% Oxide	0.11	0.06
CO ₂	% Oxide	1.18	2.34
Arsenic	μg/g	4.1	15.2
Barium	μg/g	1750	259
Boron	μg/g	200	180
Bromide	μg/g	<10	<10
Cadmium	μg/g	<1.0	1.3
Chloride	μg/g	100	180
Chromium	μg/g	21.5	27.7
Copper	μg/g	37.4	13.0
Lead	μg/g	8.4	10.8
Mercury	μg/g	<0.4	<0.4
Molybdenum	μg/g	44.4	27.7
Nickel	μg/g	466	22.1
Selenium	μg/g	2.5	2.7
Silver	μg/g	<1.0	<1.0
Vanadium	μg/g	1210	41.9
Yttrium	μg/g	10.3	6.8
Zinc	μg/g	44.0	131
Zirconium	μg/g	74.3	32.2

TABLE 12

Trace Element Suite for Initial Characterization of AFBC Residues

RCRA Elements	PIXE Elements	Other Elements
Arsenic	Copper	Boron
Barium	Molybdenum	Chlorine
Cadmium	Nickel	Sulfur
Chromium*	Rubidium	
Lead*	Vanadium	
Mercury	Yttrium	
Selenium*	Zinc	
Silver	Zirconium	

* Also identified in PIXE results.

TABLE 13

Bulk Mineralogical Characterization Results

Sample Description	Mineralogical Phases Present	Nominal Composition
TVA/Shawnee	Lime Quartz Hematite Calcite Anhydrite	CaO SiO ₂ Fe ₂ O ₃ CaCO ₃ CaSO ₄
Black Dog 1	Anhydrite Lime Calcite Portlandite Quartz	CaSO ₄ CaO CaCO ₃ Ca(OH) ₂ SiO ₂

TABLE 14

Conditioned AFBC Residues Submitted for Leaching Characterization and Trace Element Mobility Investigations

Residue	Moisture Content (%)	Curing Times (day)
Black Dog 1	37	1, 7, 14, 28
Black Dog 1	47	1, 7, 14, 28
TVA/Shawnee	20	1, 7, 14, 28
TVA/Shawnee	30	1, 7, 14, 28

Figure 12. Sampling locations of conditioned residue test cylinders.

and the second was dried and crushed for potential use in future leaching characterization study. A split of the material prepared for the leaching characterization was ground to -60 mesh for mineralogical investigations to be performed in conjunction with the leaching. All these samples have been retained and are being stored pending future funding for a leaching characterization study. The leaching characterization proposed was determined to be beyond the scope of this subtask. Additional sample preparation was required for the trace element mobility studies. The cylinder section that was reserved for this purpose had samples drilled out of specific regions of the slice using a carborundum drill bit. A sample was obtained from the center of the slice, from the edge or perimeter of each slice, and from a concentric ring between the two samples. The sampling locations are shown in Figure 12. This protocol resulted in three distinct samples for each conditioned sample that was submitted. A carborundum bit was chosen because any contamination of the samples by the drill bit would be readily recognized during the mineralogical characterization of these samples. Following this sample preparation procedure, forty-eight samples of conditioned residues were submitted for analysis of total trace elements and major/minor inorganic constituents analysis. These same samples were submitted for x-ray diffraction to identify mineralogical phases present and for comparison of the mineralogy of the conditioned versus nonconditioned material. Mineralogy was determined on the 1- and 28-day cured, conditioned materials at both moisture levels investigated in the engineering study under this task. X-ray diffraction results are listed in Table 15. Chemical analysis results of the residue from Black Dog are included in Tables 16 through 19. Tables 20 through 23 list the chemical analysis results of the residue from TVA/Shawnee. These results are presented in two different formats to ease the interpretation. The first set groups the

TABLE 15
Summary Page Ash Conditioning
NMAL XRD Analysis

1-Day	28-Day
NSP Black Dog Ash 37% H ₂ O	
Quartz (SiO ₂)	Quartz (SiO ₂)
Calcite (CaCO ₃)	Portlandite (Ca[OH] ₂)
Portlandite (Ca[OH] ₂)	Anhydrite (CaSO ₄)
Anhydrite (CaSO ₄)	Gypsum (CaSO ₄ ·2H ₂ O)
	Ettringite (Ca ₆ Al ₂ [SO ₄] ₃ [OH] ₁₂ ·26H ₂ O)
NSP Black Dog Ash 47% H ₂ O	
Quartz (SiO ₂)	Quartz (SiO ₂)
Portlandite (Ca[OH] ₂)	Portlandite (Ca[OH] ₂)
Anhydrite (CaSO ₄)	Anhydrite (CaSO ₄)
Gypsum (CaSO ₄ ·2H ₂ O)	Gypsum (CaSO ₄ ·2H ₂ O)
TVA Shawnee 20% H ₂ O	
Quartz (SiO ₂)	Quartz (SiO ₂)
Calcite (CaCO ₃)	Calcite (CaCO ₃)
Portlandite (Ca[OH] ₂)	Portlandite (Ca[OH] ₂)
Anhydrite (CaSO ₄)	Anhydrite (CaSO ₄)
Hematite (Fe ₂ O ₃)	Hematite (Fe ₂ O ₃)
	Gypsum (CaSO ₄ ·2H ₂ O)
TVA Shawnee 30% H ₂ O	
Quartz (SiO ₂)	Quartz (SiO ₂)
Calcite (CaCO ₃)	Calcite (CaCO ₃)
Portlandite (Ca[OH] ₂)	Portlandite (Ca[OH] ₂)
Anhydrite (CaSO ₄)	Anhydrite (CaSO ₄)
Hematite (Fe ₂ O ₃)	Hematite (Fe ₂ O ₃)
	Gypsum (CaSO ₄ ·2H ₂ O)

TABLE 16

Chemical Analysis of NSP/Black Dog Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	Al mg/g	Ba mg/g	Ca mg/g	Cl μg/g	Fe mg/g	Mg mg/g	Na mg/g	S %	Sr μg/g	Ti mg/g	V mg/g
37% H ₂ O 1-Day Center	22	1.6	230	93	13	11	3.6	6.3	860	1.1	1.1
37% H ₂ O 1-Day Middle	21	1.6	230	99	13	11	3.7	6.4	860	1.1	1.2
37% H ₂ O 1-Day Edge	21	1.6	230	120	13	13	4.2	6.6	840	1.1	1.1
37% H ₂ O 7-Day Center	23	1.7	250	110	13	12	3.6	6.4	880	1.1	1.2
37% H ₂ O 7-Day Middle	21	1.7	230	96	13	11	3.9	6.4	810	1.0	1.2
37% H ₂ O 7-Day Edge	22	1.6	230	120	12	11	3.8	6.2	830	1.1	1.2
37% H ₂ O 14-Day Center	23	1.7	240	96	14	11	3.8	6.4	830	1.2	1.2
37% H ₂ O 14-Day Middle	23	1.6	240	93	14	12	4.1	6.5	850	1.9	1.1
37% H ₂ O 14-Day Edge	25	1.7	230	96	14	12	4.0	6.2	870	2.0	1.2
37% H ₂ O 28-Day Center	23	1.7	230	86	14	12	3.2	6.4	870	1.8	1.2
37% H ₂ O 28-Day Middle	23	1.6	230	82	13	11	3.3	6.3	850	1.7	1.1
37% H ₂ O 28-Day Edge	22	1.6	220	110	14	11	3.7	6.2	870	1.8	1.1
47% H ₂ O 1-Day Center	24	1.7	240	78	14	13	3.9	6.3	930	2.0	1.2
47% H ₂ O 1-Day Middle	21	1.7	240	82	14	11	3.7	6.5	870	1.8	1.2
47% H ₂ O 1-Day Edge	23	1.6	230	100	13	13	3.8	6.4	840	1.9	1.2
47% H ₂ O 7-Day Center	22	1.7	220	110	13	12	3.5	6.5	840	1.3	1.2
47% H ₂ O 7-Day Middle	21	1.6	240	100	12	11	3.8	6.5	790	1.1	1.2
47% H ₂ O 7-Day Edge	22	1.7	240	100	15	13	3.6	6.3	860	2.0	1.2
47% H ₂ O 14-Day Center	22	1.6	220	120	13	12	3.7	6.3	810	1.3	1.3
47% H ₂ O 14-Day Middle	21	1.6	230	100	14	12	3.8	6.6	790	1.2	1.3
47% H ₂ O 14-Day Edge	22	1.7	250	99	13	12	3.7	6.4	840	1.1	1.2
47% H ₂ O 28-Day Center	22	1.7	240	130	14	12	3.7	6.3	840	1.4	1.2
47% H ₂ O 28-Day Middle	23	1.7	240	110	14	12	3.8	6.2	860	2.0	1.2
47% H ₂ O 28-Day Edge	22	1.7	240	110	15	13	3.6	6.4	850	2.0	1.1

TABLE 17

Chemical Analysis of NSP/Black Dog Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	As μg/g	Cr μg/g	Cu μg/g	Pb μg/g	Mn μg/g	Mo μg/g	Ni μg/g	Se μg/g	Y μg/g	Zn μg/g	Zr μg/g
37% H ₂ O 1-Day Center	6.1	21	28	7.5	170	43	410	4.7	11	54	36
37% H ₂ O 1-Day Middle	5.4	25	30	11	170	50	440	4.7	12	53	37
37% H ₂ O 1-Day Edge	6.1	23	28	8.1	170	49	440	4.2	11	48	38
37% H ₂ O 7-Day Center	9.0	24	28	3.9	170	49	440	4.3	11	55	35
37% H ₂ O 7-Day Middle	7.0	23	28	7.6	170	43	450	4.8	12	46	40
37% H ₂ O 7-Day Edge	4.6	24	27	8.0	170	44	450	4.4	12	48	38
37% H ₂ O 14-Day Center	11	24	27	8.8	170	46	450	5.5	12	52	38
37% H ₂ O 14-Day Middle	6.2	23	27	4.6	160	48	430	3.0	11	50	53
37% H ₂ O 14-Day Edge	7.6	23	29	5.6	170	44	440	3.5	11	52	31
37% H ₂ O 28-Day Center	5.5	23	30	9.1	170	48	460	3.6	11	68	40
37% H ₂ O 28-Day Middle	4.9	24	28	7.5	170	42	440	3.0	11	57	35
37% H ₂ O 28-Day Edge	5.4	20	28	7.4	160	44	440	3.1	11	56	27
47% H ₂ O 1-Day Center	5.7	24	30	6.5	180	49	460	4.3	12	53	40
47% H ₂ O 1-Day Middle	7.0	23	28	6.4	170	48	440	4.8	11	57	33
47% H ₂ O 1-Day Edge	7.7	22	29	6.3	170	46	450	5.0	12	53	38
47% H ₂ O 7-Day Center	5.0	22	37	10	160	48	430	4.4	12	47	43
47% H ₂ O 7-Day Middle	7.1	26	38	10	170	49	440	4.6	13	47	43
47% H ₂ O 7-Day Edge	6.0	25	39	10	170	50	430	4.3	12	49	40
47% H ₂ O 14-Day Center	5.8	24	39	12	190	48	450	4.6	12	64	44
47% H ₂ O 14-Day Middle	6.4	23	39	9.7	170	50	440	3.5	12	54	41
47% H ₂ O 14-Day Edge	5.4	23	37	10	160	46	390	4.0	12	42	35
47% H ₂ O 28-Day Center	6.0	25	36	9.4	160	46	430	3.9	12	43	40
47% H ₂ O 28-Day Middle	5.7	23	35	15	150	48	750	3.5	12	42	41
47% H ₂ O 28-Day Edge	5.3	21	34	10	150	44	400	4.1	12	42	37

TABLE 18

Chemical Analysis of NSP/Black Dog Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	Al mg/g	Ba mg/g	Ca mg/g	Cl μg/g	Fe mg/g	Mg mg/g	Na mg/g	S %	Sr μg/g	Ti mg/g	V mg/g
37% H ₂ O 1-Day Center	22	1.6	230	93	13	11	3.6	6.3	860	1.1	1.1
37% H ₂ O 7-Day Center	23	1.7	250	110	13	12	3.6	6.4	880	1.1	1.2
37% H ₂ O 14-Day Center	23	1.7	240	96	14	11	3.8	6.4	830	1.2	1.2
37% H ₂ O 28-Day Center	23	1.7	230	86	14	12	3.2	6.4	870	1.8	1.2
47% H ₂ O 1-Day Center	24	1.7	240	78	14	13	3.9	6.3	930	2.0	1.2
47% H ₂ O 7-Day Center	22	1.7	220	110	13	12	3.5	6.5	840	1.3	1.2
47% H ₂ O 14-Day Center	22	1.6	220	120	13	12	3.7	6.3	810	1.3	1.3
47% H ₂ O 28-Day Center	22	1.7	240	130	14	12	3.7	6.3	840	1.4	1.2
37% H ₂ O 1-Day Middle	21	1.6	230	99	13	11	3.7	6.4	860	1.1	1.2
37% H ₂ O 7-Day Middle	21	1.7	230	96	13	11	3.9	6.4	810	1.0	1.2
37% H ₂ O 14-Day Middle	23	1.6	240	93	14	12	4.1	6.5	850	1.9	1.1
37% H ₂ O 28-Day Middle	23	1.6	230	82	13	11	3.3	6.3	850	1.7	1.1
47% H ₂ O 1-Day Middle	21	1.7	240	82	14	11	3.7	6.5	870	1.8	1.2
47% H ₂ O 7-Day Middle	21	1.6	240	100	12	11	3.8	6.5	790	1.1	1.2
47% H ₂ O 14-Day Middle	21	1.6	230	100	14	12	3.8	6.6	790	1.2	1.3
47% H ₂ O 28-Day Middle	23	1.7	240	110	14	12	3.8	6.2	860	2.0	1.2
37% H ₂ O 1-Day Edge	21	1.6	230	120	13	13	4.2	6.6	840	1.1	1.1
37% H ₂ O 7-Day Edge	22	1.6	230	120	12	11	3.8	6.2	830	1.1	1.2
37% H ₂ O 14-Day Edge	25	1.7	230	96	14	12	4.0	6.2	870	2.0	1.2
37% H ₂ O 28-Day Edge	22	1.6	220	110	14	11	3.7	6.2	870	1.8	1.1
47% H ₂ O 1-Day Edge	23	1.6	230	100	13	13	3.8	6.4	840	1.9	1.2
47% H ₂ O 7-Day Edge	22	1.7	240	100	14	13	3.6	6.3	860	2.0	1.2
47% H ₂ O 14-Day Edge	22	1.7	250	99	13	12	3.7	6.4	840	1.1	1.2
47% H ₂ O 28-Day Edge	22	1.7	240	110	15	13	3.6	6.4	850	2.0	1.1

TABLE 19

Chemical Analysis of NSP/Black Dog Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	As μg/g	Cr μg/g	Cu μg/g	Pb μg/g	Mn μg/g	Mo μg/g	Ni μg/g	Se μg/g	Y μg/g	Zn μg/g	Zr μg/g
37% H ₂ O 1-Day Center	6.1	21	28	7.5	170	43	410	4.7	11	54	36
37% H ₂ O 7-Day Center	9.0	24	28	3.9	170	49	440	4.3	11	55	35
37% H ₂ O 14-Day Center	11	24	27	8.8	170	46	450	5.5	12	52	38
37% H ₂ O 28-Day Center	5.5	23	30	9.1	170	48	460	3.6	11	68	40
47% H ₂ O 1-Day Center	5.7	24	30	6.5	180	49	460	4.3	12	53	40
47% H ₂ O 7-Day Center	5.0	22	37	10	160	48	430	4.4	12	47	43
47% H ₂ O 14-Day Center	5.8	24	39	12	190	48	450	4.6	12	64	44
47% H ₂ O 28-Day Center	6.0	25	36	9.4	160	46	430	3.9	12	43	40
37% H ₂ O 1-Day Middle	5.4	25	30	11	170	50	440	4.7	12	53	37
37% H ₂ O 7-Day Middle	7.0	23	28	7.6	170	43	450	4.8	12	46	40
37% H ₂ O 14-Day Middle	6.2	23	27	4.6	160	48	430	3.0	11	50	53
37% H ₂ O 28-Day Middle	4.9	24	28	7.5	170	42	440	3.0	11	57	35
47% H ₂ O 1-Day Middle	7.0	23	28	6.4	170	48	440	4.8	11	57	33
47% H ₂ O 7-Day Middle	7.1	26	38	10	170	49	440	4.6	13	47	43
47% H ₂ O 14-Day Middle	6.4	23	39	9.7	170	50	440	3.5	12	54	41
47% H ₂ O 28-Day Middle	5.7	23	35	15	150	48	750	3.5	12	42	41
37% H ₂ O 1-Day Edge	6.1	23	28	8.1	170	49	440	4.2	11	48	38
37% H ₂ O 7-Day Edge	4.6	24	27	8.0	170	44	450	4.4	12	48	38
37% H ₂ O 14-Day Edge	7.6	23	29	5.6	170	44	440	3.5	11	52	31
37% H ₂ O 28-Day Edge	5.4	20	28	7.4	160	44	440	3.1	11	56	27
47% H ₂ O 1-Day Edge	7.7	22	29	6.3	170	46	450	5.0	12	53	38
47% H ₂ O 7-Day Edge	6.0	25	39	10	170	50	430	4.3	12	49	40
47% H ₂ O 14-Day Edge	5.4	23	37	10	160	46	390	4.0	12	42	35
47% H ₂ O 28-Day Edge	5.3	21	34	10	150	44	400	4.1	12	42	37

TABLE 20

Chemical Analysis of TVA/Shawnee Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	Al mg/g	Ba mg/g	Ca mg/g	Cl μg/g	Fe mg/g	Mg mg/g	Na mg/g	S %	Sr μg/g	Ti mg/g	V μg/g
20% Mix9 1-Day Center	18	0.38	350	110	45	14	0.48	5.3	420	0.87	47
20% Mix9 1-Day Middle	19	0.33	350	110	49	14	0.41	5.4	430	0.93	45
20% Mix9 1-Day Edge	18	0.29	350	110	46	14	0.59	5.5	450	0.88	43
20% Mix7 7-Day Center	15	0.31	350	100	44	14	0.42	5.5	450	0.78	39
20% Mix7 7-Day Middle	16	0.28	350	110	44	14	0.37	5.4	450	0.77	40
20% Mix7 7-Day Edge	16	0.26	360	110	41	14	0.38	5.5	460	0.69	37
20% Mix4 14-Day Center	16	0.27	360	120	41	14	0.37	5.5	430	0.73	38
20% Mix4 14-Day Middle	16	0.34	350	100	41	13	0.35	5.4	430	0.76	37
20% Mix4 14-Day Edge	16	0.24	360	110	40	14	0.37	5.6	440	0.73	37
20% Mix1 28-Day Center	16	0.36	360	90	41	14	0.35	5.6	430	0.67	36
20% Mix1 28-Day Middle	16	0.26	360	94	40	13	0.37	5.5	410	0.68	36
20% Mix1 28-Day Edge	16	0.26	360	96	41	14	0.54	5.6	460	0.70	35
30% Mix8 1-Day Center	15	0.24	300	100	31	13	0.41	5.6	430	0.53	39
30% Mix8 1-Day Middle	17	0.21	320	100	39	14	0.42	5.5	390	0.48	38
30% Mix8 1-Day Edge	16	0.21	320	110	38	14	0.43	5.5	410	0.48	39
30% Mix6 7-Day Center	17	0.22	320	100	37	13	0.38	5.5	450	0.44	39
30% Mix6 7-Day Middle	16	0.19	320	100	34	14	0.41	5.5	390	0.40	39
30% Mix6 7-Day Edge	16	0.30	310	110	42	13	0.41	5.6	430	0.88	38
30% Mix5 14-Day Center	17	0.31	320	100	45	14	0.44	5.5	430	0.88	39
30% Mix5 14-Day Middle	17	0.27	310	100	45	13	0.39	5.6	410	0.88	39
30% Mix5 14-Day Edge	17	0.28	330	96	45	14	0.50	5.6	420	0.86	38
30% Mix3 28-Day Center	17	0.35	340	90	45	14	0.39	5.6	450	0.81	37
30% Mix3 28-Day Middle	16	0.38	350	82	43	14	0.57	5.5	430	0.82	37
30% Mix3 28-Day Edge	16	0.22	340	100	41	13	0.36	5.5	420	0.76	38

TABLE 21

Chemical Analysis of TVA/Shawnee Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	As μg/g	Cr μg/g	Cu μg/g	Pb μg/g	Mn μg/g	Mo μg/g	Ni μg/g	Se μg/g	Y μg/g	Zn μg/g	Zr μg/g
20% Mix9 1-Day Center	13	25	17	12	110	27	24	2.2	8.5	150	22
20% Mix9 1-Day Middle	13	27	18	11	110	28	25	2.3	7.8	150	16
20% Mix9 1-Day Edge	14	26	17	13	110	28	26	2.2	8.3	160	19
20% Mix7 7-Day Center	13	25	18	10	110	26	26	1.6	7.8	180	17
20% Mix7 7-Day Middle	14	26	16	11	110	28	25	1.8	8.4	130	18
20% Mix7 7-Day Edge	14	25	14	8.9	110	28	27	2.4	7.6	150	17
20% Mix4 14-Day Center	14	25	13	11	110	28	25	1.9	8.1	130	19
20% Mix4 14-Day Middle	14	24	13	8.9	110	27	26	1.4	7.3	130	13
20% Mix4 14-Day Edge	15	24	13	9.3	110	27	23	2.0	7.5	140	24
20% Mix1 28-Day Center	14	23	12	9.6	110	30	24	1.3	7.9	150	17
20% Mix1 28-Day Middle	13	23	14	9.2	100	26	24	1.8	7.8	120	14
20% Mix1 28-Day Edge	13	23	13	8.9	100	25	23	2.0	7.1	150	14
30% Mix8 1-Day Center	14	23	12	16	110	27	23	3.8	8.4	140	10
30% Mix8 1-Day Middle	15	24	12	15	110	24	24	4.8	8.6	150	12
30% Mix8 1-Day Edge	13	26	12	15	110	27	26	3.8	8.3	130	3
30% Mix6 7-Day Center	12	27	14	15	110	29	27	3.9	9.1	120	12
30% Mix6 7-Day Middle	14	25	12	15	110	26	25	3.8	8.8	130	12
30% Mix6 7-Day Edge	14	25	17	15	110	29	24	2.7	7.7	130	21
30% Mix5 14-Day Center	15	26	15	11	110	26	23	2.4	7.5	130	21
30% Mix5 14-Day Middle	14	25	13	13	110	29	24	2.4	8.4	120	18
30% Mix5 14-Day Edge	13	24	16	12	100	26	22	2.3	8.2	130	22
30% Mix3 28-Day Center	16	25	18	11	100	27	23	1.6	8.2	130	21
30% Mix3 28-Day Middle	14	24	16	11	110	25	24	2.0	8.1	130	20
30% Mix3 28-Day Edge	13	25	16	11	110	27	25	1.6	8.3	120	21

TABLE 22

Chemical Analysis of TVA/Shawnee Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	Al mg/g	Ba mg/g	Ca mg/g	Cl μg/g	Fe mg/g	Mg mg/g	Na mg/g	S %	Sr μg/g	Ti mg/g	V μg/g
20% Mix9 1-Day Center	18	0.38	350	110	45	14	0.48	5.3	420	0.87	47
20% Mix7 7-Day Center	16	0.31	350	100	44	14	0.42	5.5	450	0.78	39
20% Mix4 14-Day Center	16	0.27	360	120	41	14	0.37	5.5	430	0.73	38
20% Mix1 28-Day Center	16	0.36	360	90	41	14	0.35	5.6	430	0.67	36
30% Mix8 1-Day Center	15	0.24	300	100	31	13	0.41	5.6	430	0.53	39
30% Mix6 7-Day Center	17	0.22	320	100	37	13	0.38	5.5	450	0.44	39
30% Mix5 14-Day Center	17	0.31	320	100	45	14	0.44	5.5	430	0.88	39
30% Mix3 28-Day Center	17	0.35	340	90	45	14	0.39	5.6	450	0.81	37
20% Mix9 1-Day Middle	19	0.33	350	110	49	14	0.41	5.4	430	0.93	45
20% Mix7 7-Day Middle	16	0.28	350	110	44	14	0.37	5.4	450	0.77	40
20% Mix4 14-Day Middle	16	0.34	350	100	41	13	0.35	5.4	430	0.76	37
20% Mix1 28-Day Middle	16	0.26	360	94	40	13	0.37	5.5	410	0.68	36
30% Mix8 1-Day Middle	17	0.21	320	100	39	14	0.42	5.5	390	0.48	38
30% Mix6 7-Day Middle	16	0.19	320	100	34	14	0.41	5.5	390	0.40	39
30% Mix5 14-Day Middle	17	0.27	310	100	45	13	0.39	5.6	410	0.88	39
30% Mix3 28-Day Middle	16	0.38	350	82	43	14	0.57	5.5	430	0.82	37
20% Mix9 1-Day Edge	18	0.29	350	110	46	14	0.59	5.5	450	0.88	43
20% Mix7 7-Day Edge	16	0.26	360	110	41	14	0.38	5.5	460	0.69	37
20% Mix4 14-Day Edge	16	0.24	360	110	40	14	0.37	5.6	440	0.73	37
20% Mix1 28-Day Edge	16	0.26	360	96	41	14	0.54	5.6	460	0.70	35
30% Mix8 1-Day Edge	16	0.21	320	110	38	14	0.43	5.5	410	0.48	39
30% Mix6 7-Day Edge	16	0.30	310	110	42	13	0.41	5.6	430	0.88	38
30% Mix5 14-Day Edge	17	0.28	330	96	45	14	0.50	5.6	420	0.86	38
30% Mix3 28-Day Edge	16	0.22	340	100	41	13	0.36	5.5	420	0.76	38

TABLE 23

Chemical Analysis of TVA/Shawnee Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	As μg/g	Cr μg/g	Cu μg/g	Pb μg/g	Mn μg/g	Mo μg/g	Ni μg/g	Se μg/g	Y μg/g	Zn μg/g	Zr μg/g
20% Mix9 1-Day Center	13	25	17	12	110	27	24	2.2	8.5	150	22
20% Mix7 7-Day Center	13	25	18	10	110	26	26	1.6	7.8	180	17
20% Mix4 14-Day Center	14	25	13	11	110	28	25	1.9	8.1	130	19
20% Mix1 28-Day Center	14	23	12	9.6	110	30	24	1.3	7.9	150	17
30% Mix8 1-Day Center	14	23	12	16	110	27	23	3.8	8.4	140	10
30% Mix6 7-Day Center	12	27	14	15	110	29	27	3.9	9.1	120	12
30% Mix5 14-Day Center	15	26	15	11	110	26	23	2.4	7.5	130	21
30% Mix3 28-Day Center	16	25	18	11	100	27	23	1.6	8.2	130	21
20% Mix9 1-Day Middle	13	27	18	11	110	28	25	2.3	7.8	150	16
20% Mix7 7-Day Middle	14	26	16	11	110	28	25	1.8	8.4	130	18
20% Mix4 14-Day Middle	14	24	13	8.9	110	27	26	1.4	7.3	130	13
20% Mix1 28-Day Middle	13	23	14	9.2	100	26	24	1.8	7.8	120	14
30% Mix8 1-Day Middle	15	24	12	15	110	24	24	4.8	8.6	150	12
30% Mix6 7-Day Middle	14	25	12	15	110	26	25	3.8	8.8	130	12
30% Mix5 14-Day Middle	14	25	13	13	110	29	24	2.4	8.4	120	18
30% Mix3 28-Day Middle	14	24	16	11	110	25	24	2.0	8.1	130	20
20% Mix9 1-Day Edge	14	26	17	13	110	28	26	2.2	8.3	160	19
20% Mix7 7-Day Edge	14	25	14	8.9	110	28	27	2.4	7.6	150	17
20% Mix4 14-Day Edge	15	24	13	9.3	110	27	23	2.0	7.5	140	24
20% Mix1 28-Day Edge	13	23	13	8.9	100	25	23	2.0	7.1	150	14
30% Mix8 1-Day Edge	13	26	12	15	110	27	26	3.8	8.3	130	3
30% Mix6 7-Day Edge	14	25	17	15	110	29	24	2.7	7.7	130	21
30% Mix5 14-Day Edge	13	24	16	12	100	26	22	2.3	8.2	130	22
30% Mix3 28-Day Edge	13	25	16	11	110	27	25	1.6	8.3	120	21

various curing times for all points in a slice of the original sample cylinder at a single moisture level. The second set groups the results by location of the drill site in the original cylinder over time at a single moisture level.

The chemical analyses results, in conjunction with the mineralogical results, indicate that the mobility of elemental constituents in conditioned AFBC residues is virtually nondetectable. Results of the total chemical analysis are the same within the variability of the analytical method and the heterogeneous nature of these residues. Statistical analysis of these results was not performed, as general observations were adequate to conclude that the mobility of major, minor, and trace element constituents was very low even at the lowest curing times and moisture contents. Even the most mobile constituents, such as chloride and sodium, showed no trend of mobility in this study. The only mineralogical changes that were noted between 1-day curing and 28 days of curing was the formation of gypsum, which is a hydrated form of CaSO_4 . Anhydrite, the nonhydrated form of CaSO_4 , was present in the sample at 1-day curing time in all cases. Only one sample, the Black Dog AFBC at 37% moisture, showed the development of ettringite ($\text{Ca}_6\text{Al}_2[\text{SO}_4]_3[\text{OH}]_{12} \cdot 26\text{H}_2\text{O}$) in the sample that had cured for 28 days.

Leaching characterization of these conditioned materials is planned at a future date. The leaching characterization will include short- and long-term leaching procedures. This study will provide extremely beneficial supplemental information when complete.

3.3 Bituminous Coal Fly Ash Data Collection and Evaluation

3.3.1 Introduction

The Western Fly Ash Research, Development, and Data Center (WFARDDC) is a research group funded by a consortium of sponsors interested in the utilization and safe economical disposal of coal by-products. A major research effort since the initiation of the WFARDDC has been the development of a database of information on the physical, chemical, and mineralogical properties of low-rank coal by-products, primarily fly ash. A database, such as the one generated by the WFARDDC, provides a valuable source of scientific and engineering information. The format is useful in identifying trends and specific information pertinent to current and potential utilization applications as well as disposal scenarios and research projects involving coal by-products. The current version of the Western Fly Ash Database contains entries representing more than 500 samples of low-rank coal by-products. WFARDDC researchers have begun a statistical evaluation of the information in this database. Information continues to be entered into the database, and the evaluation process is continuing. The initial evaluation of the database has provided valuable information regarding low-rank coal by-products and has initiated interest in researchers, electric power utilities, coal by-products marketers, and others to extend the database to include similar information on bituminous coal by-products. Bituminous coal fly ash is of particular interest due to the high volume of this material utilized and disposed, primarily in the midwest and eastern United States. A database of information on bituminous coal fly ash has the potential to provide information valuable to the electric utility industry as it strives to meet regulatory mandates, such as the Clean Air Act, by blending coal and utilizing alternate coal combustion methods and by-product collection systems.

The effort to collect and evaluate physical, chemical, and mineralogical information on bituminous coal fly ash will result in a database that can be merged with the current Western Fly Ash Database or be utilized as a stand-alone database. As with the current database, the information will not identify the by-products by electric utility or company affiliation to guarantee anonymity to the participants in this effort.

Interaction with utilities, coal ash marketers and end users, as well as research groups in the areas of coal combustion technologies and environmental systems, has indicated a strong interest in the characteristics of solid by-products or residues from advanced coal combustion technologies. In order to facilitate a scientific and engineering understanding of the characteristics of these materials, this task was expanded to include the development of a database of information on the physical, chemical, and mineralogical characteristics of advanced coal process residues. This preliminary investigation will provide information on which standard engineering and analytical tests are applicable and what new or innovative testing may provide more valuable and predictive information. It will also provide a basis for comparison of the residues generated by various technologies with each other and conventional solid by-products.

3.3.2 Objective and Scope

The primary objective of this task is to collect and evaluate information on the physical, chemical, and mineralogical properties of bituminous coal fly ash and to generate a database of this information. Information of this type that is unavailable through identified sources will need to be generated at the EERC's laboratory facilities. Research staff in the Coal By-Products Utilization Laboratory (CBUL), Analytical Research Laboratory (ARL), and the Natural Materials Analytical Laboratory (NMAL) have extensive experience in both standard testing protocols and numerous research projects on coal conversion by-products, including continuing WFARDDC efforts. These laboratories are equipped with state-of-the-art instrumentation and have extensive analytical and testing capabilities.

The availability of information of interest for the proposed database will be assessed through other research organizations, such as the Electric Power Research Institute, electric power utilities, coal ash marketers, and other groups associated with the coal by-products industry. The inquiries for this information will include mainly sources in the United States; however, foreign sources will be used where readily available. The information will be collected from voluntary participants. Information that is unavailable will be generated at the EERC's facilities from samples of bituminous coal fly ash submitted by identified participants. The evaluation phase of this task allows for the identification of additional information for inclusion in the database as the task continues. A database will be generated; however, the nature of this task implies that the database content and format will evolve over the time frame of the task. A bituminous coal fly ash database will be assembled in a final form for distribution at the conclusion of this task, but it is expected that expansion of the database will continue as has been the case with the Western Fly Ash Database.

An additional objective for the final year of this task is to assemble a database of information on residues from advanced coal processes. The work plan is similar in scope and format to the workplan on bituminous coal fly ash. There will be two major differences in the effort: 1) evaluation of current characterization methods as they apply to advanced coal process residues and development of new methods/techniques where required, and 2) a majority of the samples for inclusion in the database will be obtained from research projects at the EERC or from the Department of Energy (DOE).

3.3.3 Bituminous Coal Fly Ash Data Collection and Evaluation Results

The primary objective of this task--to collect and evaluate information on the physical, chemical, and mineralogical properties of bituminous coal fly ash--is a long-term objective that will continue for the EERC coal by-products research group well past the end of this task. During the time frame of this specific task, the primary objective has been met to the expected level. The primary end result of this effort has been the construction of a database of information on bituminous coal fly ash. The construction of the database also provided opportunities to relate the by-product properties and production to the overall coal-fired electric power generation facility. As a result, several observations can be made that should significantly impact the overall understanding of the coal combustion by-product utilization industry, the by-product disposal practices, the functional relationships within a utility, and the impact of research in these areas. These observations, coupled with the technical expertise required to generate the characterization information for the database and the database itself, should provide useful insight for the research community to address important waste management issues.

A preliminary hard copy version of the Lotus® 1-2-3® spreadsheet format of the bituminous coal fly ash database is included in this report as Appendix A. A key defining the terms used in the spreadsheet is also included in Appendix A. The components of the database as included in this report are the major and minor elemental constituents (expressed as oxides), mineral phases identified in the crystalline portion of the fly ash, selected physical properties and test results relevant to the utilization of fly ash as a mineral admixture in concrete, and information on the operating system and coal source.

The chemical characterization information consists of two groups. The first is the results as dictated by the American Society for Testing and Materials (ASTM) C618 (1991). The chemical composition information required by ASTM to classify fly ash is the total concentration of silicon, aluminum, iron, sulfur, and calcium. Magnesium, sodium, and potassium are included in the ASTM procedures as alternate information. These have also been included in the database for as many samples as possible. Test results from the ASTM designated procedures for moisture (mass of water lost at 105°-110°C), loss on ignition (LOI, mass lost at 750°C), and available alkali (soluble sodium and potassium reported as equivalents of Na₂O) are also included in the database. The second portion of the chemical information in the database includes total concentrations of other minor elemental constituents. These elements were phosphorus, titanium, barium, manganese, and strontium. In keeping with the ASTM convention for reporting the concentrations of major elements in fly ash,

all major and minor elemental concentrations were calculated and reported as the common oxides. ASTM also requires the sum of the SiO_2 , Al_2O_3 , and Fe_2O_3 values for evaluation under C618. This value is also included in the database under "Sum." Table 24 lists all elemental constituents included in the chemical characterization scheme and the common oxide form used for reporting purposes.

TABLE 24
Elemental Constituents Analyzed in Fly Ash and
Common Oxides Used for Reporting Purposes

Element	Common Oxide
ASTM C618 Requirements	
Silicon	SiO_2
Aluminum	Al_2O_3
Iron	Fe_2O_3
Sulfur	SO_3
Calcium	CaO
Alternate ASTM C618 Tests	
Magnesium	MgO
Sodium	Na_2O
Potassium	K_2O
Minor Elemental Constituents	
Phosphorus	P_2O_5
Titanium	TiO_2
Barium	BaO
Manganese	MnO_2
Strontium	SrO

In the physical portion of the database, the tests performed were fineness (325 sieve test), specific gravity, pozzolanic activity test with portland cement (28 day), pozzolanic activity with lime (7 day), water requirement, and autoclave expansion. These tests are also included in the ASTM C618 "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan as a Mineral Admixture in Portland Cement Concrete." These procedures were performed in accordance with ASTM C311 (1990).

Fly ash mineralogy was determined by a semiquantitative x-ray powder diffraction protocol developed by Dr. Gregory McCarthy at North Dakota State University (McCarthy et al., 1990). This method uses the "Reference Intensity Ratio," where rutile (TiO_2) is the internal intensity standard. Fly ash is composed of crystalline and amorphous or glassy phases. X-ray diffraction only identifies the crystalline phases. Future research may include the use of scanning electron microscopy point count (SEMP) to determine the chemistry of the amorphous phases. Crystalline phases, mineralogy codes, and nominal chemical compositions are included in Table 25.

TABLE 25

Crystalline Phases, Mineralogy Codes, and Nominal Chemical Compositions

Crystalline Phase	Mineralogy Code	Composition
Anhydrite	Ah	CaSO_4
Tricalcium Aluminate	C3A	$\text{Ca}_3\text{Al}_2\text{O}_6$
Hematite	Hm	Fe_2O_3
Lime	Lm	CaO
Melilite	Ml	$\text{Ca}_2(\text{Mg},\text{Al})(\text{Al},\text{Si})_2\text{O}_7$
Mullite	Mu	$\text{Al}_6\text{Si}_2\text{O}_{13}$
Merwinite	Mw	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$
Periclase	Pc	MgO
Quartz	Qz	SiO_2
Ferrite Spinel	Sp	$(\text{Mg},\text{Fe})(\text{Fe},\text{Al})_2\text{O}_4$

Ash fusion was also performed on most samples represented in the database. The ash fusion procedure was performed according to ASTM D1857 (1968), and ash fusion temperatures in both an oxygen atmosphere (O_2) and a reducing atmosphere (CO_2) were generated. The test requires marking various temperatures as a preformed triangular pyramid (cone) passes through certain defined stages of fusing and flow when heated at a specified rate in controlled atmospheres. There are four stages to this fusing:

1. Initial deformation temperature (IT): the first rounding of the apex of the cone
2. Softening temperature (ST): the cone has fused down to a spherical lump in which the height is equal to the width at the base

3. Hemispherical temperature (HT): the cone has fused down to a hemispherical lump at which the height is one half the width of the base
4. Fluid temperature (FT): the fused mass has spread out in a nearly flat layer with a maximum height of 1/16 inch

The ideal cone shape for each of the critical temperature points is shown in Figure 13. Ash fusion temperatures are useful in determining ash behavior in boilers and potentially for use of these materials in high-temperature utilization technologies.

As noted earlier in this section, some important observations regarding the understanding of the coal combustion by-product utilization industry, the by-product disposal practices, the functional relationships within a utility, and the impact of research in these areas, were made over the duration of this task. These observations can be summarized as follows:

- Coal combustion fly ash is an underutilized resource in the United States. Government agencies, utilities, and research organizations need to coordinate efforts to promote ash use in current proven applications and extend ash use to new markets and applications.
- ASTM has set standards and specifications for the use of coal combustion fly ash in specific applications; however, these standards and specifications can be misleading and may be misapplied. Industry and research groups need to continue participation in ASTM committee work to maintain appropriate standards and to develop new and improved standards and specifications where needed.

Figure 13. Critical temperature points and associated cone shapes for ash fusion test procedure (ASTM D1857).

- Regulatory agencies should encourage the use of coal combustion fly ash in proven applications. The use of coal combustion fly ash is consistent with the current emphasis on reuse and recycle. The use of this high-quality and lower-cost material can provide an economic advantage in rebuilding and expanding the U.S. infrastructure.
- Coal combustion fly ash should not be categorized as a waste material when it is utilized in engineering or other applications. Coal combustion fly ash should only be designated as a waste in the event the material requires disposal.
- Coal combustion fly ash must not be compared to, or confused with, fly ash resulting from the combustion of other materials, such as municipal solid waste or refuse. It is incorrect and inappropriate to regulate "ash" as a single type of material.
- Coal-fired electric generation facilities need to consider the production of coal combustion fly ash and other solid residues as an additional product resulting from their operations. This will become particularly advantageous as additional environmental restrictions are placed on air emissions and solid waste disposal. Production of a usable and salable solid residue will be highly advantageous.
- Conventional coal fly ash will likely change in character as advanced coal combustion techniques, clean coal technologies, and new emissions control technologies become more prevalent. These new characteristics need to be investigated for utilization potential immediately to fit them into the current market and develop new markets for the future.

3.3.4 Advanced Coal Process Residues Database Results

A preliminary spreadsheet database of information on residues from various advanced coal processes has been generated. The effort involved required to complete this database is beyond the scope of this task; however, identifying and characterization information available at the EERC, through past and ongoing research projects involving these "new" coal conversion residues, has been collected and placed in a Lotus® 1-2-3® spreadsheet as the initial step toward constructing a complete database similar in scope to the coal combustion fly ash database (which now includes the bituminous coal fly ash database). As the required characterization and identifying information needed for the advanced coal process residues database is identified and obtained, this additional database will be formalized and eventually connected to the coal combustion fly ash database.

Part of the effort required to begin generating reliable and reproducible mineralogical characterization information on advanced coal process residues was to develop a semiquantitative x-ray powder diffraction technique. The protocol was developed by Dr. Gregory McCarthy at North Dakota State University under a subcontract to the EERC. The protocol uses the Reference Intensity Ratio, which requires mixing a fixed amount of an internal standard with each residue. Rutile (TiO_2), the internal standard used for coal combustion fly ash, produced peaks overlapping with analytical peaks of the new phases in the advanced coal process residues. An alternative internal standard, zinc oxide (ZnO), was identified.

3.4 Waste Depository Scavenger Study

3.4.1 Introduction

The initial goal of the Waste Depository Scavenger task was to develop a blend of scavenging materials, such as zeolite and clay minerals and chars, which have a high potential to inhibit the migration of mobile contaminants from certain types of waste depositories. These materials would be incorporated into landfills, possibly within the liners, and would be composed of the most appropriate scavenging agents, depending on the leachate contaminants present in the depository. Appropriate sampling and analysis of these scavenging materials would provide a means to reconstruct contaminant migration in both vertical and horizontal directions.

Constructing large depositories for municipal and industrial waste has become a standard waste management practice. Monitoring potentially hazardous leachate migrating from a waste depository is a critical responsibility to prevent groundwater and soil contamination. Current monitoring techniques, which consist of sampling and analysis of materials around the depository, are inadequate. This type of analysis can be inaccurate due to the heterogeneity of the materials and the virtually undetectable compositional changes with time.

Contaminants emanating from municipal waste include lead, copper, zinc, and, contaminants migrating from fly ash waste include boron, molybdenum, arsenic, and selenium. Remediation of these types of contaminants is expensive and sometimes problematic. Inexpensive waste-cell liners composed of abundant natural materials could be an economical way to immobilize contaminants.

Ion exchange in zeolites has been studied and documented in the literature. Clinoptilolite, a common zeolite, is a framework aluminosilicate mineral with the general formula $(\text{Na},\text{K})_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$. Clinoptilolite and many other zeolites occur mainly in microcrystalline sedimentary masses which usually form by the reaction of pore water with volcanic material. Relatively large windows (which are several angstroms wide) or "channels" within the clinoptilolite structure easily hold large ions. The ion exchange capabilities of clinoptilolite have been extensively studied, mainly because of its ability to scavenge cesium¹³⁷ from radioactive waste and ammonium ions from municipal waste (Mercer and Ames, 1978). Clinoptilolite is stable to a pH of less than 2, which is important if the scavenging material will be exposed to weathering processes.

3.4.2 Research Scope

A two-phase test plan was used to determine contaminant migration and sorptive capacity of the scavenger materials. The first phase involved the evaluation of structural and chemical properties of the proposed scavenger materials. The second phase involved the use of batch testing and percolation experiments to determine contaminant sorption of the scavenger. The proper composite mixture of scavenging agents for optimum immobilization of a variety of contaminants will be addressed in the continuation of this research.

Initially, the clinoptilolite was tested for its ability to immobilize ions such as selenium, molybdenum, copper, and lead. Common municipal landfill contaminant ions of lead and copper were chosen for initial experiments because clinoptilolite has a strong affinity for both of these ions. Selenium and molybdenum were chosen for the first percolation experiment because they are common constituents in fly ash leachate. These ions were also selected because they are soluble in water and can be easily detected with the analytical tools at our disposal. Initial funding for this task was limited; therefore, testing of clay minerals for the adsorption of cations and testing of chars or lignites for the adsorption of organics have not been initiated. In subsequent testing, these scavenging materials will be combined and tested for their ability to immobilize a variety of contaminants found in waste depositories.

3.4.3 Results

3.4.3.1 Initial Materials Characterization

Initially, samples of zeolites from the Sentinel Butte and Bullion Creek Formations of western North Dakota were targeted for utilization in these experiments. Mineralogical characterization using XRD indicated that these samples were composed mainly of analcime. Analcime is not capable of efficient ion exchange at ambient temperatures, so this material was not utilized in this research.

Clinoptilolite from East West Minerals Company, Denver, Colorado, was analyzed by XRD to determine other phases present and was found to be nearly homogeneous, with only a minor amount of quartz. The XRD results indicated that the clinoptilolite has a structure similar to sodium-rich zeolites, but SEM/EPMA revealed that the zeolite was more potassium- than sodium-rich (Table 26). This indicates that XRD data should be compared to SEM/EPMA analyses to properly determine the chemical constituents of a crystalline phase. Often XRD peaks may be shifted due to sample preparation techniques or instrumentation settings. Photomicrographs were taken to document the morphology of the crystals.

For the percolation experiments, 20 wt% of the clinoptilolite and 80 wt% of the silica sand was mixed to obtain a permeable material. A portion of the original clinoptilolite/sand mixture was submitted for XRF analysis to determine if trace amounts of selenium or molybdenum were present in the mixture. No molybdenum was detected, but selenium was present in small amounts, probably in quantities less than 10 ppm. The presence of selenium in the clinoptilolite/sand mixture indicates that the material may be suitable for scavenging selenium. The percolation tests will determine if this hypothesis is correct.

TABLE 26

SEM/EPMA Results for Clinoptilolite (Normalized Weight Percents)

No.	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	MgO	MnO	CaO	Na ₂ O	K ₂ O	Label
1	76.06	13.44	0.00	0.47	0.34	0.00	1.09	2.52	6.08	x-91-183.1
2	76.35	13.32	0.00	0.43	0.42	0.00	0.54	2.60	6.34	x-91-183.2
3	75.81	11.93	0.36	3.94	0.46	0.00	1.22	1.03	4.86	x-91-183.3
4	76.61	13.70	0.00	0.41	0.64	0.53	0.48	3.33	4.30	x-91-183.4
5	77.73	12.46	0.00	0.00	0.23	0.35	0.89	1.40	5.75	x-91-183.5
6	71.22	12.25	0.40	4.29	2.97	0.24	1.96	1.77	4.47	x-91-183.6
7	75.81	12.13	0.00	1.57	0.47	0.00	1.73	0.28	6.74	x-91-183.7
8	74.81	10.79	1.24	4.02	0.40	1.01	1.45	0.22	6.07	x-91-183.8
9	77.51	12.18	0.00	0.51	0.42	0.59	1.02	1.79	4.95	x-91-183.9
10	79.93	12.52	0.29	0.76	0.28	0.00	0.53	1.28	3.92	x-91-183.10

3.4.3.2 Batch Experiments

After the initial characterization of the materials, the next phase of this research was to determine the amount of contaminants that the clinoptilolite could immobilize. Initial "batch" testing involved reacting the clinoptilolite with a small portion of a solution containing contaminant species. The first tests used a 1 M (molar) solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. This high concentration of copper would not normally be found in a field setting, but was used to allow for easy detection of changes in weight between samples. Copper sulfate was used because of its high solubility in water.

For these batch experiments, one gram of clinoptilolite was added to 10 mL of the copper solution. The sample was then shaken by a mechanical mixer (a Spex mill which is commonly used to attrition samples for XRD analysis) for varying lengths of time to allow the solution and solid to reach equilibrium. The analysis of the samples revealed that when the clinoptilolite and solution were shaken for 1 hour, a noticeable attritioning of grains and the formation of clay-sized particles occurred. Subsequent analysis of these attritioned samples showed that they did not immobilize the copper as efficiently as the samples that had been shaken for only 40 minutes. This difference may be due to the destruction, during shaking, of open channels within the clinoptilolite where the copper would be adsorbed. When nonattritioned, the clinoptilolite can immobilize a large amount of copper from solution.

Lead is another common constituent found in municipal waste leachate and was used for the next set of batch experiments. A 1 wt% solution of $\text{Pb}(\text{NO}_3)_2$ and distilled-deionized water was reacted with the clinoptilolite using the same "batch" testing method as used for the copper sulfate solution. The reacted and unreacted samples were submitted for inductively coupled argon plasma (ICAP) analysis, which is used to determine the concentration of ions in solution.

The unreacted (control) sample contained approximately 6800-ppm (parts per million) lead in solution (Table 27). The reacted sample indicated that the clinoptilolite immobilized approximately 98% of the lead out of solution. This ability of clinoptilolite to scavenge copper and lead out of solution is a very promising characteristic that may lead to utilization of this material in municipal waste depository liners.

TABLE 27
Results from the Batch Test for Lead

Parameter	Initial (ppm)	Final (ppm)
Na ⁺¹	1580	1430
Pb ⁺²	6780	102
NO ₃ ⁻¹	3800	3800

3.4.3.3 Percolation Experiments

The next phase of the project included the completion and setup of one percolation test cell (Figure 14). Sampling ports, which will allow periodic sampling of the percolating solution, were drilled and sealed. Because of the cost of silica beads, an alternative material, a silica sand (97% SiO₂), was chosen to be mixed with the clinoptilolite within the test cell to increase the permeability of the material. The silica sand was analyzed using XRD to determine other constituents, which included plagioclase and potassium feldspars.

The next phase of the waste depository scavenger task will involve the actual percolation experiment. A solution containing 100-ppb selenium and 100-ppb molybdenum with a basic pH (11 to 11.5), to simulate leachate commonly found in fly ash landfills, will be percolated through the clinoptilolite/silica material. Sampling of the solution will occur at regular intervals. Water analyses of the percolating solution will be performed at the ARL using atomic absorption spectroscopy. Several XRD analyses will be performed on the scavenging materials at the completion of the percolation experiment. The XRD results will be compared to the original characterization of the materials to determine changes within the structure of the mineral phases present. These results may indicate if the crystal structure of the clinoptilolite is altered during the percolation experiment.

Some question still remains as to the proper valence states of selenium and molybdenum. For both elements, valence states of +6 were chosen because they represent the most frequently occurring forms of these elements in a fly ash depository, under oxidizing conditions. The selenium/molybdenum solution and the test cell are being prepared for the percolation experiments.

Figure 14. Percolation test cell.

3.4.4 Future Research

The next phase of this project will involve the use of clinoptilolite, a clay, and an activated lignite or char in percolation laboratory test cells. A solution containing several common contaminant constituents in concentrations that would simulate a waste depository leachate setting will be used. The scavenging agents will be packed in layers with more permeable materials interspersed to reduce the time to complete the percolation experiment. The leachate will be collected at regular intervals for water analyses, and the scavenging materials will be analyzed using XRD after completion of the percolation tests.

Development of North Dakota clinoptilolites for use in both present and future experiments will be pursued. Some of the samples collected early in this project from the Killdeer Mountains area of North Dakota were thought to contain bentonite, a clay-containing deposit, but mineralogical characterization by XRD showed them to contain calcite and clinoptilolite. This material could possibly be utilized in future experiments.

Additionally, experimentation to develop methods or treatments to increase the ion-exchange capacity of the scavenging materials in an effort to maximize their efficiency of immobilizing contaminants will be explored. Future research will focus on determining the quantities of contaminants that are permanently immobilized, the quantities that are able to be remobilized from the scavenging agents, and any mineral structural changes that occur during the ion exchange process. This analysis will be useful to characterize the stability of the contaminant-containing scavenging material. The end goal

of this task will be to supply the necessary information that will support or oppose the hypothesis that different scavenging materials possess qualities that suit those materials for specific contaminant immobilization. By combining a few selected scavenging materials, an optimum mix will be developed to immobilize several contaminants at a specific site.

4.0 REFERENCES

- ASTM C311-90, Method for sampling and testing fly ash or natural pozzolan for use as a mineral admixture in portland cement concrete: Vol. 04.02, Concrete and aggregates.
- ASTM C618-91, Specification for fly ash and raw or calcined natural pozzolan for use as a mineral admixture in portland cement concrete: Vol. 04.02, Concrete and aggregates.
- ASTM D1857-68, Test method for fusibility of coal and coke ash: Vol. 05.05, Gaseous fuels, coal, and coke.
- Bazzel, C.E., and Mallory, R.G., 1987, Disposal of multicyclone and baghouse catch at TVA's 20-MW AFBC pilot plant: Tennessee Valley Authority, West Paducah, KY, p. 967-973.
- Bland, A.E., Jones, C.E., Rose, J.G., and Harness, J.L., 1989, Ash management options for AFBC: p. 323-333.
- Golden, D., 1988, EPRI R&D on AFBC solid waste management: Current status and future direction.
- Grady, C.P.L., Jr., and Lim, H.C., 1980, Biological wastewater treatment: Theory and applications: Marcel Dekker, Inc., New York, NY.
- McCarthy, G.J.; Solem, J.K.; Manz, O.E.; Hassett, D.J., 1990, Use of a database of chemical, mineralogical and physical properties of North American fly ash to study the nature of fly ash and its utilization as a mineral admixture in concrete, *In* Day, R.L. and Glasser, R.P., eds., *Proceedings of Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal VI*: Vol. 178, p. 3-33.
- Mercer, B.W., and Ames, L.L., 1978, *Zeolite exchange in radioactive and municipal wastewater treatment*, *In* Sand, L.B., and Mumpton, F.A., eds., *Natural zeolites: Occurrence, properties, use*: London, Pergamon Press, p. 451-462.
- Reynolds, Tom D., 1982, Unit operations and processes in environmental engineering: Brooks/Cole Engineering Division, Monterey, CA,
- RP 2708-1, 1988, Concept design guidelines for atmospheric fluidized combustion waste management: EPRI CS-6053 Final Report, December 1988, Prepared by Baker/TSA, Inc., Coraopolis, Pennsylvania, and ICF Technology Inc., Richland, Washington, Sections 3, 5, 7, 8.

Smith, I.M., 1989, Management of AFBC residues: Draft Report, IEA Coal Research, August 1989.

Standard methods for the examination of water and wastewater, 16th Ed.: American Public Health Association, Washington D.C., 1985.

Suidan, M.T. et al., 1987, Anaerobic wastewater treatment, final report: Fossil Energy Publication, DOE/MC/21281-2562, Department of Energy, Nov.

Wark, K., and Warner, C.F., 1981, Air pollution: Its origin and control, 2d ed.: New York, Harper and Row Publishers, p. 219-233.

APPENDIX A
BITUMINOUS COAL FLY ASH DATABASE

SOURCE OF COAL	BOILER TYPE/MANUFACTURER	PARTICULATE REMOVAL	COAL TYPE	CBUI NO.	ASTM C 618 Chemical Compositions (wt%)										ADDITIONAL CHEMICAL DATA						
					SiO2	Al2O3	Fe2O3	Sum	SO3	CaO	MgO	H2O	LOI	AA	Na2O	K2O	P2O5	TiO2	BaO	MnO2	SrO
KY, E.VA.	PC TANGENTIAL/RS	ESPRC	BIT	81.0219	47.70	33.60	12.40	93.70	0.45	1.00	0.90	0.08	3.42	0.41							
EMERY CO.,UTAH		ESPBUELL	BIT	82.0202	59.30	20.00	3.70	83.00	0.38	6.50	2.30	0.06	2.85								
EAST KENTUCKY		ESPIAMSTAND&CARB.	BIT	82.0354	62.30	17.60	4.30	84.20	1.33	3.30	0.90	0.09	10.22	1.31	1.50	1.10					
EAST KENTUCKY		ESPIAMSTAND&CARB.	BIT	82.0355	65.30	16.70	4.20	86.20	1.20	4.00	1.10	0.06	7.66	1.35	1.60	1.20					
KY, E.VA.	PC TANGENTIAL/RS	ESPRC	BIT	82.0361	51.20	24.60	9.80	85.60	0.38	1.40	0.90	0.04	4.33	0.39							
BALDWIN, IL		ESPRC	BIT	83.0062	50.90	19.20	16.50	86.60	1.10	6.20	1.20	0.07	0.78	0.69	0.72	1.95					
EAST KENTUCKY		ESPIAMSTAND&CARB.	BIT	83.0106	54.70	29.90	4.50	89.10	0.27	1.10	0.80	0.19	4.99	0.45	0.27	2.55					
KY, E.VA.	PC TANGENTIAL/RS	ESPRC	BIT	83.0157	49.20	29.90	8.90	88.00	0.40	1.90	0.80	0.05	5.03	0.46							
KY, E.VA.	PC TANGENTIAL/RS	ESPRC	BIT	83.0257	48.30	29.90	8.20	86.40	0.43	1.60	0.70	0.09	5.68	0.46							
IL., IN		ESPBUELL	BIT	83.0509	50.00	22.30	13.70	86.00	1.65	3.60	1.40	0.24	1.36	0.98	0.84	2.74					
E.KY, VA.	PC TANGENTIAL/RS	ESPRC	BIT	84.0033	49.20	29.50	9.00	87.70	0.50	1.70	1.00	0.10	4.65	0.55							
UTAH		ESP&MULTIARC	BIT	85.0238	51.40	10.60	8.40	70.40	1.62	21.20		0.40	1.00	0.33							
WYOMING		ESP&MULTIARC&LC	BIT	85.0239	58.50	18.20	7.40	84.10	0.70	7.40		0.32	0.26	0.38							
PENNSYLVANIA		BAGHOUSE/CARB.	BIT	85.0241	48.00	26.30	10.40	84.70	0.85	1.60		0.16	5.92	0.29							
PENNSYLVANIA		ESPRC&BUELL	BIT	85.0242	48.50	28.50	13.90	90.90	0.98	1.60		0.24	4.83	0.22							
PENNSYLVANIA		ESPIWESTERN&RC	BIT	85.0243	49.60	28.30	13.30	91.20	1.35	1.40		0.90	3.63	0.21							
BALDWIN, IL		ESPRC	BIT	85.0327	50.20	18.70	15.80	84.70	1.15	15.80	1.00	0.15	0.62	0.70	0.90	2.00					
PENNSYLVANIA		BAGHOUSEWF	BIT	86.0235	58.70	26.40	6.20	91.30	0.35	1.00	0.90	0.07	3.37	0.74	0.40	2.50					
PENNSYLVANIA		ESPIWESTERN	BIT	86.0993	47.70	26.90	12.00	86.60	0.09	2.70		0.23	2.25	0.25							
EMERY CO.,UTAH		BIINFLAKT	BIT	86.0998	63.00	19.90	3.60	86.50	0.75	5.40		0.01	2.12	0.62							
ARIZONA		ESPRC	BIT	86.1175	55.70	21.50	5.40	82.60	0.42	8.00		0.02	1.83	0.67							
EAST KENTUCKY		ESPIAMSTAND&CARB.	BIT	87.0002	65.30	18.20	3.60	87.10	0.38	5.90		0.04	0.88	0.76							
EMERY CO.,UTAH		WET VENTURI	BIT	87.0025	61.00	18.30	3.30	82.60	0.48	5.70		0.03	4.54	0.86							
EMERY CO.,UTAH		BIINFLAKT	BIT	87.0026	59.80	19.80	3.90	83.50	0.78	5.90		0.04	3.30	0.69							
EAST KENTUCKY		ESPIAMSTAND&CARB.	BIT	87.0038	66.50	16.60	4.50	87.60	0.32	5.20		0.05	0.26	0.76							
MANSFIELD, LA		ESPIUOP	BIT	87.0157	52.77	23.63	8.87	85.27	0.36	9.50	2.67	0.02	0.01	1.64	1.09	0.84					
PA., OH., KY., WV.	DRY BOTTOM/B&W	ESPIWESTERN	BIT	90.0198	49.80	25.20	15.20	90.20	0.83	2.27	0.91	0.11	1.92	0.67	0.46	2.20					
CLINCHFIELD COAL		ESPIKOPPERS	BIT	90.0199	49.50	26.30	7.75	83.55	0.98	5.50	1.75	0.06	1.13	1.15	0.50	3.23					
CZECHOSLOVAKIA	N/A	N/A	BIT	90.0200	57.20	25.30	8.48	90.98	0.27	1.95	1.22	0.16	1.00	0.81	0.31	1.44					
WOLFE CREEK	CYCLONE/RS	ESPBUELL	BIT	90.0201	48.40	30.50	7.97	86.87	1.02	2.39	0.83	0.20	3.35	0.91	0.41	2.11					
N/A	N/A	N/A	BIT	90.0202	52.20	20.10	8.39	80.69	0.75	3.07	1.51	0.11	10.30	0.83	0.15	1.77					
PENNSYLVANIA		ESPIWESTERN	BIT	90.0203	49.00	27.40	11.90	88.30	0.90	2.45	0.91	0.12	2.60	0.60	0.24	2.34					
MARRIBONE	CYCLONE/FW	ESPIBELCO	BIT	90.0204	56.20	32.00	3.13	91.33	0.16	0.66	0.90	0.02	2.65	1.00	0.79	2.72					
IL., WY	PC	ESPILC	BIT	91.0042	45.57	21.15	7.92	74.64	1.30	15.72	3.28	0.01	0.48	0.70	0.91	1.27	0.70	1.37	0.41	0.04	0.26
IL., WY	PC	ESPILC	BIT	91.0043	48.58	20.25	9.13	77.96	0.97	12.27	2.84	0.01	1.34	0.87	1.00	1.80	0.40	1.29	0.25	0.05	0.21
IL., WY	CYCLONE	ESPRC	BIT	91.0052	42.76	17.56	19.20	79.52	1.60	4.49	1.32	0.34	3.52	1.42	1.35	2.95	0.21	1.35	0.07	0.04	0.05
IL., WY	CYCLONE	ESPRC	BIT	91.0053	39.18	15.16	16.36	70.70	1.60	4.94	1.03	0.16	18.85	0.62	0.70	1.80	0.19	0.95	0.05	0.04	0.04
MARRIBONE	CYCLONE/FW	ESPIBELCO	BIT	91.0086	58.02	32.00	3.17	93.19	0.15	0.65	0.83	0.05	2.07	0.65	0.22	2.69	0.07	1.45	0.06	0.02	0.04
WOLFE CREEK	CYCLONE/C-E	ESPBUELL	BIT	91.0087	56.47	28.53	6.51	91.51	0.23	0.64	1.19	0.02	4.41	0.84	0.44	3.56	0.05	1.12	0.07	0.03	0.04
WOLFE CREEK	CYCLONE/RS	ESPBUELL	BIT	91.0088	54.77	30.62	6.62	92.01	0.32	0.86	0.78	0.05	3.56	0.53	0.24	2.26	0.05	1.34	0.06	0.04	0.05
OH, KY, WV	PC_OPPPOSED WALL/B&W	ESPBUELL	BIT	91.0130	58.30	26.80	6.27	91.37	0.39	1.30	1.01	0.13	1.68	1.14	0.31	2.73	0.26	1.76	0.10	0.02	0.09
OH, KY, WV	PC_OPPPOSED WALL/B&W	ESPBUELL	BIT	91.0131	57.50	26.10	6.16	89.76	0.68	1.26	0.98	0.24	4.77	1.48	0.30	2.63	0.28	1.71	0.11	0.02	0.09
OH, KY, WV	PC_OPPPOSED WALL/B&W	ESPBUELL	BIT	91.0132	59.90	25.10	7.58	92.58	0.23	1.73	0.95	0.06	2.91	0.88	0.29	2.47	0.21	1.59	0.10	0.04	0.09
OH, KY, WV	PC_OPPPOSED WALL/B&W	ESPBUELL	BIT	91.0133	60.20	25.50	7.81	93.51	0.27	1.70	0.99	0.07	2.23	0.58	0.31	2.55	0.23	1.61	0.10	0.04	0.10
OH, KY, WV	PC_OPPPOSED WALL/B&W	ESPBUELL	BIT	91.0134	58.20	25.20	7.06	90.46	3.97	1.08	0.82	0.11	2.12	0.75	0.26	2.28	0.12	1.52	0.10	<0.01	0.08
OH, KY, WV	PC_OPPPOSED WALL/B&W	ESPBUELL	BIT	91.0135	59.40	25.40	7.95	92.75	2.74	1.13	0.86	0.10	3.30	1.09	0.24	2.18	0.13	1.52	0.10	<0.01	0.08
OH, KY, WV	PC_OPPPOSED WALL/B&W	ESPBUELL	BIT	91.0136	59.40	25.30	8.23	92.93	0.32	1.83	0.93	0.08	1.66	1.21	0.31	2.47	0.09	1.46	0.11	0.01	0.08
OH, KY, WV	PC_OPPPOSED WALL/B&W	ESPBUELL	BIT	91.0137	58.70	24.40	7.62	90.72	0.28	1.66	0.88	0.08	1.45	0.63	0.30	2.48	0.09	1.42	0.10	0.01	0.09
KOREA		N/A	BIT	91.0138	57.87	25.07	4.07	87.01	0.17	3.37	1.02	0.06	5.28	0.35	0.23	1.34					
KOREA		N/A	BIT	91.0139	38.37	20.83	5.38	64.58	0.51	0.47	0.60	1.06	29.60	0.28	0.12	3.01					
E.KY., VA., WV.		ESPRC	BIT	91.0174	53.40	30.00	5.76	89.16	0.04	2.06	0.98	0.08	0.91	0.61	0.31	2.07					
KY E., VA, WV		ESP&MULTIARC	BIT	91.0179	49.60	26.90	6.69	83.19	0.44	1.44	1.07	0.07	6.82	1.04	0.08	2.61					
E.KY, VA.	PC TANGENTIAL/RS	ESPRC	BIT	91.0183	53.97	26.05	10.73	90.75	0.40	2.30	1.21	0.10	3.76	0.99	0.45	2.35	0.34	1.15	0.20	0.02	0.16
E.KY, VA.	PC TANGENTIAL/RS	ESPRC	BIT	91.0184	52.44	26.19	11.81	90.44	0.50	2.64	1.32	0.10	4.57	1.07	0.49	2.36	0.36	1.48	0.20	0.03	0.16
E.KY.		ESPIC-E	BIT	91.0185	53.15	27.95	9.52	90.62	0.45	1.65	1.65	0.16	3.14	1.06	0.38	2.65	0.69	1.45	0.14	0.02	0.15
E.KY.		ESPIC-E	BIT	91.0186	55.04	28.22	8.74	92.00	0.42	1.69	1.14	0.12	2.93	1.04	0.42	2.63	0.63	1.41	0.14	0.02	0.15
PEOPLES REP. CHINA	N/A	N/A	BIT	91.0208	56.18	28.60	5.30	90.08	0.62	3.46	0.89	0.11	5.41	*	0.35	1.14					

13. Signature of Recipient and Date <i>David R. Hagan</i> 07/28/92	14. Signature of DOE Reviewing Representative and Date
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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Waste Management (2.2)		3. Reporting Period 4-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Water and Waste Resource Management:				
a.1.	HWD CWF process water treatability testing	6-30-92			
a.2	Activated carbon evaluation	6-30-92			
Task B	Coal Combustion Ash Conditioning Study	1-31-92	2-29-92		
Task C	Collection, Generation, and Evaluation of Bituminous Coal Ash Data Base	6-30-92			
Task D	Waste Depository Scavenger	6-30-92			
Task E	Environmental Mercury Associated with Fossil Fuel Utilization	6-30-92		Task E was not initiated due to lack of funding upon completion of Task B.	
Task F	Preparation of Six-Year Final Report	8-31-92			

2.3 Regional Energy Policy Program for the Northern Great Plains

REGIONAL ENERGY POLICY PROGRAM FOR THE NORTHERN GREAT PLAINS

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

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July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

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REGIONAL ENERGY POLICY PROGRAM FOR THE NORTHERN GREAT PLAINS

1.0 INTRODUCTION

The United States is the world's leading consumer of energy. The production and consumption of energy vary over the country as a function of climate, the availability of natural resources, economics, and culture. The northern Great Plains region (Montana, Wyoming, North Dakota, and South Dakota), an area characterized by many similarities in climate, culture, and physiography:

- Accounts for over 10 percent of domestic hydrocarbon production; a major share of low-rank, low-sulfur coal production; and a significant amount of steam-generated electricity.
- Contains significant oil shale, geothermal, nuclear, and conventional fossil fuel resources.
- Contains significant research capability, particularly with regard to coal-conversion and oil shale technologies, and, with respect to the environmental effects of fossil fuel production, conversion and utilization.
- Is a net exporter of energy and fossil fuel materials.
- Is a significant consumer of fuel and fossil fuel by-products in the agricultural sector.
- Receives significant revenues and economic support from fossil fuel exploration, production, conversion, and transportation industries, as well as from ancillary industries.

2.0 PROGRAM OBJECTIVES

Energy-related activities are significant in the economy at the regional, state, and local levels. Fluctuations in energy markets can have marked effects on government revenues and programs, as well as on the economy. Since the end of the World War II, the northern Great Plains has experienced economic "boom" cycles related to oil and gas, coal, oil shale, hydroelectric power, and uranium. Since the early 1970s, energy markets have reacted to an increase in environmental awareness and the growth and diversification of energy sources and suppliers on a global scale. For example, during that time, the region's coal sector was affected by the nature of regulatory actions with respect to air quality and waste management.

National Energy Strategy (NES) development is underway that is attempting to take into account the mix of environmental, fiscal, social, research, economic, national security, and resource issues that form the energy picture of the nation. Ensuring the optimal production and utilization of the region's energy resources, within the framework of the developing NES, could be enhanced by responses and initiatives both at the state and regional levels. Once the basic framework of the strategy is in place, periodic review of the policy with respect to the region would be augmented by ready access to

pertinent data on the regional level. To this end, the objectives of the Regional Energy Policy Program for the Northern Great Plains, as originally proposed, were to:

- Gather, develop, and disseminate information necessary for well-founded energy initiatives in the region.
- Promote and assist in the integration and coordination of the energy-planning efforts of individual states in the region.
- Foster communication between the public and private sector concerning energy-planning needs in the region.
- Achieve objectives and carry out activities in a manner consistent with the NES.

The mission of the Energy Policy Program for the Northern Great Plains can best be achieved through an information center which provides background on major issues, supporting materials, and a catalogue of information sources, including agencies, groups, database services, and pertinent activities. The program is proceeding in this direction with the development of the "Energy Policy Information Center" (EPIC) for the northern Great Plains.

3.0 YEAR 3--SECOND BIENNIAL PERIOD: GOALS/ACTIVITIES

The choice of a GIS® information management system during the reporting period for data management required a reevaluation of the approach and scope of work for the project. First, the use of the GIS® database, a fully relational data system, removed the need to develop Lotus® or other spreadsheet systems for the data as originally envisioned under Tasks C, D, and E.

Secondly, organization of the data for entry and manipulation proved most efficient in the following groups: production, facilities, consumption and markets, waste generation and management, resources and reserves, and taxation and revenue. Data entry and map development were initiated for "production" and "facilities" during this reporting period (Attachment A).

Third, GIS® systems require a geographic tie in order to store and manipulate data. The county was chosen as the appropriate level of portrayal for the information for the following reasons:

- It is a geographic entity common to geologic, political, regulatory and industry information.
- It allows the ready treatment both of variables with large populations, such as producing wells, as well as groups with lesser populations, such as Class II wells or mines.
- It provides an adequate number of data points, that is, individual counties, to portray information at the state, county, geologic province, or regional level.

With smaller data sets, the capability exists to post specific locations with accompanying information.

3.1 Task A. Development of an Information Management System

Objective The objective of Task A is to develop an integrated data management system for the storage, organization, and manipulation of data, as well as allowing for varied output including graphics, such as maps, tables, and reports. Activities under this task include identifying data types and desired product formats, surveying available software (including capabilities and potential for interaction), and obtaining software for testing and, if appropriate, use. In addition, activities include identification and acquisition of appropriate computer hardware.

Accomplishments Activities to January of 1992 focused on the acquisition and testing of hardware and software. Accomplishments included:

- Identification and acquisition of appropriate computer hardware for testing and eventual use with a range of software packages (9/89).
- Identification, acquisition, testing, and application of software packages, including the following:
 - Lotus 3.1 for numerical data (3/90)
 - Q&A, a flat file manager, for databases containing text and requiring sorting (i.e., annotated bibliography) (9/89)
 - Atlas GIS® system (acquisition, 12/90; partial evaluation, first quarter '91)
 - MapViewer by Golden Software (obtained, evaluated, and approved as the database shell and was subsequently purchased for approximately \$250)

During this reporting period the following occurred:

- A programmer was hired to supervise database design, data entry, data management and output design.
- A reevaluation of data management systems resulted in the selection of Atlas GIS® as the data management package (see the March monthly report).
- Atlas GIS® software was acquired. Computer hardware needed to accommodate the Atlas GIS® system, including upgraded hard drives and a desk jet printer, was identified and acquired.
- Atlas GIS® was tested using information from the natural gas test set. This was followed by the development of an overall database format, general data entry, and the production of map products as part of the development of a comprehensive database for energy-related information for the northern Great Plains (NGPCOMP; see Attachment A).

As outlined in the March monthly report, products for Tasks C, D, E, and F are now included as data sets with supporting documentation in the Atlas GIS® NGPCOMP database.

3.2 Task B. Information Acquisition

3.2.1 Subtask B.1 Annotated Bibliography of Energy-Related Sources

Objective The objective of this activity is to develop a computer-based annotated bibliography of key sources with respect to the various energy-related subject areas in the northern Great Plains. Information sources include trade and lobbying groups, company reports, and state and legislative agencies. Activities include the identification, acquisition, review, entry, and indexing of sources.

Accomplishments Activities to January 1992 included:

- Acquisition of Q&A software.
- Design of input and report formats.
- Identification and acquisition of energy-related sources for the northern Great Plains, including computerized databases, organizations, federal and state governments, and libraries.
- Input into the Q&A system, consisting of a bibliographic entry, key words, and, following an evaluation of the source, a review and any additional key words and information.
- Housing of reference materials. Discussions were initiated regarding the housing of these reference materials as a specific collection within the library system at the University of North Dakota.
- Identification of key references by sector (1/92)
 - Coal
 - Oil
 - Gas

During this reporting period, the following activities were undertaken:

- Identification of key references by sector
 - Electricity (1/92)
 - Nuclear (2/92)
 - Biofuels (2/92)
 - Geothermal (2/92)
 - Hydropower (2/92)
 - Oil shale (2/92)

3.2.2 Subtask B.8 Organizations Database

Objective The objective of Subtask B.8 is to develop a computerized database of key energy-related organizations for the northern Great Plains (ENERCON).

Accomplishments Prior to January 1991, selected energy-related groups at the national and regional levels were identified and contacted with respect to their activities on policy issues. The groups included environmental organizations, research organizations, government agencies, and industry trade groups. A list of organizations contacted was included as an attachment to the March 1991 monthly report. The database was completed as scheduled and included in the last semiannual report as Attachment D.

During this reporting period, **ENERCON** was maintained and updated as necessary.

3.3 Task C. Energy Resource Database

Objective The objective of this task is to develop a computerized database to provide information on current energy-related resources and determine the status of resource assessment.

Accomplishments Activities to January 1992 included:

- Identifying and acquiring data sources, mainly published reports.
- Designing and testing a Lotus® 3.1® database.
- Initiating a report dealing with the status of coal resource assessment in the region. A draft dealing with resource assessment in the Williston Basin (Fort Union Lignite Region) was submitted as an attachment to the June 1991 monthly report.

During this reporting period, the following occurred:

- Data continued to be acquired and organized for entry into the **NGPCOMP** database.
- The report on the status of resource assessment for coal, and oil/gas, and other energy sources were rescheduled for the next quarter.

3.4 Task D. Energy Production Database

Objective The objective of this task is to develop a computerized database to provide information on current energy-related production. Related databases will be prepared and will pertain to the storage, treatment, and conversion (i.e., mines, power facilities, refineries, gas processing facilities) of fuels.

Accomplishments Activities to January 1992 included:

- Identifying data sources.
- Designing and testing a production database at the state level using Lotus® 3.1.®
- Initiating a Q&A® database for coal mines in the region.
- Initiating a Q&A® database for coal conversion facilities. A sample entry was included in the April 1991 monthly report.

- Preparation of databases on coal
 - Mines (**MINE**)
 - Conversion facilities (**PLANT**)

During this reporting period, the **MINE** and **PLANT** databases were updated, QA/QC was performed, and a final product was included in the May monthly report. These databases served as the source of data in these subject areas for the Atlas GIS® **NGPCOMP** database.

3.5 Task E. Energy Consumption Database

Objective The objective of this task is to develop a computerized database to provide information on energy consumption in the region.

Accomplishments Activities to January 1992 focused on identifying data sources, acquiring data, and, in the second quarter of Year 2, designing and testing a database in Lotus® 3.1®. No activities were scheduled in this task during the last biannual period.

No activities were undertaken in this task during the current reporting period.

3.6 Task F. Energy Technology Database

Objective The objective of this task is to develop a computerized database to provide information on energy conversion and related technologies, focused on the northern Great Plains.

Accomplishments Activities to January 1992 focused on identifying data sources and acquiring data.

Activities to date have focused on the preparation of critiques dealing with low-rank coal conversion technologies based on published and in-house sources. A sample entry was included as an attachment to the April 1991 monthly report. The Q&A® **TECH** database was completed during the last biannual period.

During this reporting period information was updated.

3.7 Task G. Government Initiatives Database

Objective The objective of this task is to develop computerized databases and supporting documentation dealing with energy-related policy initiatives at the federal and state levels.

Accomplishments Activities to January 1992 focused on:

- The compilation of a concise history of energy-related events at the international, national, and regional levels.
- The identification and, where available, assessment of past federal and state policy actions in a historical context.
- Identification and tracking of current policy initiatives, and, where available, supporting documentation at the federal and state levels.

During this reporting period, tracking of federal policy developments continued and included:

- Regular contact with personnel of the congress, administration, industry associations, and research groups.
- Acquisition of published sources from USDOE, industry associations, environmental groups, and, notably, the Environmental and Energy Study Institute (Weekly Bulletin, Legislation Briefing Books, Special Reports).

During this reporting period, discussions were held with companies providing on-line policy-related information. These groups included **LEXIS/NEXIS** and **WESTLAW** (see Attachment C, January 1992 monthly).

Following an evaluation of the nature and availability of information in this area, it was decided that the products for Task G should be changed to the following:

- For Subtask G.1
 - A report entitled "History and Status of National Energy Policy" (now in draft form).
 - A database containing a concise review of federal policy initiatives during the period (currently in draft form).
- For Subtask G.2 the information would be included in Task B products as follows:
 - A summary of key published data sources to be included in **ENERBIB** (B.1)
 - A summary of other sources for inclusion in **ENERCON** (B.8).

3.8 Task H. Environmental Issues Database

Objective The objective of this task is to prepare summary reports dealing with energy-related environmental issues in the northern Great Plains region.

Accomplishments Activities to January 1992 focused on the identification and acquisition of sources and on the preparation of reports regarding:

- Surface mining of coal--the preparation of an assessment of the environmental effects of surface mining coals in the region based on published sources and current research programs.
- Lignite conversion wastes--the preparation of an assessment of the environmental effects, focused on groundwater, of the disposal of coal conversion wastes (e.g., fly ash, FGD waste, gasification waste) based on published sources and current research programs.

- Oil and gas exploration and production wastes--the preparation of an assessment of the environmental effects, particularly on the shallow subsurface, of exploration and production wastes based on published sources and current research programs. Efforts to date have focused on drilling wastes (see attachment to June 1991 monthly report).

During this reporting period, the products were rescheduled for completion during the next quarter.

4.0 TRIPS/PRESENTATIONS

No trips or presentations were made during this reporting period.

5.0 FUTURE ACTIVITIES

The revised completion date for the program is December 31, 1992. The revised program schedule will be included in the July 1992 Monthly Report.

The tasks have been revised to reflect the current focus on developing demonstration sets for the Atlas GIS® **NGPCOMP** database under Task A and the finalization of reports under Tasks C, G, and H. Revisions include:

- Database subtasks under Tasks C, D, and E; additional data gathered under H will be redirected to fulfill Subtask A.4.
- For Subtask G.1.
 - A report entitled "History and Status of National Energy Policy" (currently in draft form).
 - A database containing a concise review of federal policy initiatives during the period 1970-1980 (currently in draft form).
- For Subtask G.2-5. The product will consist of a summary of key published data sources in **ENERBIB** and other information sources in **ENERCON** as part of Task B.
- Reports under Tasks C and H have been rescheduled for the second quarter.

Section 5.0 provides a general review of future activities for the first half of Year 4.

5.1 Task A. Development of an Information Management System

Over the next biannual period, the schedule calls for the preparation of database demonstration sets as outlined in Section 3.1.

5.2 Task B. Information Acquisition

5.2.1 Subtask B.1 Annotated Bibliography of Energy-Related Sources

In the coming biannual period, work on the annotated bibliography will focus on the systematic review and rating of key sources outlined in this reporting period. Since this activity is relatively time-intensive, it will be undertaken as time allows.

5.2.2 Subtask B.2 Energy-Related Organizations Database

Activities will focus on the maintenance and enlargement of the database. A list of contacts for energy-related lobbying groups in the region, supplied by state governments, is an example of a key data set which continues to expand.

5.3 Task C. Energy Resource Database

In the coming biannual period, the schedule requires activity on determining the status of resource assessment in certain energy sectors and for developing resource databases.

The resource assessment reports will be completed in the second quarter.

Resource and reserve information will be prepared and entered into the **NGPCOMP** database.

5.4 Task D. Energy Production Database

Work in the coming biannual period will focus on the completion of the Q&A coal mine and coal conversion facility databases, particularly the information on waste generation and management.

Efforts will focus on the QA/QC of information for the **NGPCOMP** database.

5.5 Task E. Energy Consumption Database

Efforts will focus on the preparation of energy consumption data for entry into the **NGPCOMP** database.

5.6 Task F. Energy Technology Database

No work is scheduled in this task in the coming biannual period.

5.7 Task G. Government Initiatives Database

Work will focus on the following:

- Tracking policy developments at the national, regional, and state levels. Activities will include reviewing energy-related actions at the state level for the last legislative session, obtaining final bill status reports, and reviewing the changes to the state codes. At the federal level, activities will focus on tracking the various

congressional and administration energy initiatives as they move through committee and go before the Congress.

- For Subtask G.1.
 - A report entitled "History and Status of National Energy Policy" (currently in draft form).
 - A database containing a concise review of federal policy initiatives during the period 1970-1980 (currently in draft form).
- For Subtask G.2-5. Product will consist of a summary of key published data sources in **ENERBIB** and other information sources in **ENERCON** as part of Task B.

5.8 Task H. Environmental Issues Database

In the coming biannual period, work will focus on the following:

- The finalization of a summary report dealing with the status of knowledge concerning the environmental effects of coal mining in the region.
- The finalization of a summary report dealing with the status of knowledge concerning the environmental effects of coal-conversion waste management, particularly on groundwater.
- The finalization of a summary report concerning the status of knowledge of environmental effects of oil and gas exploration and production wastes in the region.
- The finalization of a draft summary report dealing with the ramifications of the 1990 Amendments to the Clean Air Act on the region, particularly with respect to coal.
- The finalization of a report dealing with issues related to leasing of federal lands.

ATTACHMENT A

STATUS OF THE NGPCOMP DATABASE

ATTACHMENT A

STATUS OF THE **NGPCOMP** DATABASE (6-30-92)

NGPCOMP (Northern Great Plains Comprehensive database) is a GIS (geographic information system) database developed under this project using Atlas GIS® software (see March '92 monthly report) which is designed to provide ready access to energy-related information for the northern Great Plains region. Information areas include resources/reserves, production, facilities, waste generation/waste management, markets and consumption, and revenue. These data reflect efforts under Tasks C through E.

The information is typically entered and displayed at the county level. In the case of data sets of less than 100 components, such as gas processing facilities or coal mines, data points are entered individually with detailed data sets, while in the case of larger data sets, such as oil or gas wells, county totals only are entered and the data are generalized.

Where possible information sources are nonproprietary and include published reports, government personnel and reports, and industry personnel, associations, and reports. Other databases developed under this project, including Mines and Plants, were used to expedite data entry.

The following contents of this attachment provide a picture of the status of **NGPCOMP** as of June 30, 1992:

A.1--Information sources for the **NGPCOMP** database

A.2--**NGPCOMP** database status (6-30-92)

A.3--**NGPCOMP** database printout

A.4--Draft maps from the **NGPCOMP** database

A.1

Information Sources for the NGPCOMP Database

	MT	ND	SD	WY
Oil				
# of Wells	3	4	2	21
Total Prod. & Yr	3	4	2	8
Gas				
# of Wells	5	4	2	5
Total Prod. & Yr	3,5	4	2	8
Water				
Total Prod. & Yr	3	4	2	21
Oil Associated	3	4	2	--
Gas Associated	3	4	2	--
Class II				
Total	5	4	2	5
EOR Wells	5	4	2	5
SWD Wells	5	4	2	5
Oil-Related Facilities				
Refineries	6	6	6	6
Pump Stations	--	--	--	--
Gas-Related Facilities				
Processing Plants	6	6	NA	6
Compress. Stations	7	7	7	7
Storage Facilities	1	NA	NA	1
Coal Mines				
Background	10,11,16	10,14,16,22	10,16,18	10,16,19,20
Production	*,11	*,14,22	NA	*,19,20
Customer Info.	*,11	*,14,22	NA	*,19
Geologic Setting	*,10,11	*,10,22	NA	*,10,19
Environmental	*,11	*,23	NA	*
Financial	*,10,11	*,10	NA	*,10,20
Generating Stations				
Background	9,10,13,15,1	9,10,12,13,1	9,10,13,17	9,10,13,17
Boiler Spec.	7	4,15,17	*,9,13,17	*,9,13,17
Average Load	*,9,13,15,17	*,9,13,15,17	*,17	*,17
Flue Gas Cleaning	*,15,17	*,15,17	*,9,13,17	*,9,13,17
Fuel Information	*,9,13,15,17	*,9,13,15,17	*,9,13,17	*,9,13,17
Waste Management	*,9,13,15,17	*,13,15,17	*	*
Customer Info.	*	*,23	*,13	*,13

NGPCOMP - SOURCE CODES
TRG - 7/21/92

Codes Sources

- * Industry Contact Person.
- 1 American Gas Association (AGA), 1988, Survey of Underground Gas Storage Facilities in the United States and Canada. Updated by Mr. James Hicks (7/92).
- 2 South Dakota Department of Environment and Natural Resources, 1991, Oil, Gas, and Water Production Second Half, 1991.
- 3 Montana Department of Natural Resources and Conservation, Oil and Gas Conservation Division, Annual Report 1990. Also Mr. Richard Jacobson, Statistician, with the above agency.
- 4 North Dakota Industrial Commission, Mr. Dave Hvinden, Analyst.
- 5 Petroleum information--Previous search.
- **6 PennWell Publishing, Oil and Gas Journal Energy Databases, 1991, Worldwide Gas Processing Survey and U.S. Refinery Survey.
- 7 PennWell Publishing, 1988, Natural Gas Pipelines of the United States and Canada, Third Edition, Map.
- 8 Wyoming Oil and Gas Conservation Commission, 1990, Oil & Gas Statistics 1990 and Wyoming Oil and Gas 1990.
- **9 Edison Electric Institute, 1989, Power Directory 1989, 405 p.
- **10 Keystone Coal Industry Manual, 1991, MacLean-Hunter Publications, 1004 p.
- 11 McCulloch, Robin, October 1991, Montana Mining Directory 1989-1990, MBMG Bulletin 129, 146 p.
- 12 Montana Department of Natural Resources and Conservation, Energy Division, December 1989, Montana Historical Energy Statistics, Sixth Edition, 88 p.
- **13 NUS Corporation, 1983, Commercial Coal Power Plants: Edition 5, 67 p.
- 14 North Dakota Public Service Commission, Siting Division, June 1985, Electric Transmission Facilities in North Dakota, Maps 1 & 2. Also, communication with NDPSC staff members.
- 15 Selle, S.J., Gronhovd, G.H., and Sondreal, E.A., 1986, Review of slagging and fouling from low-rank coals: Plant survey, bibliography, and discussion: U.S. Department of Energy, 227 p.
- 16 U.S. Department of Energy, Energy Information Administration, September 1991, Coal Production 1990, DOE/EIA-0118(90), 136p. (from Form: EIA-7A; Coal companies must complete a variety of forms and surveys in compliance with federal and state regulations.)

NGPCOMP - Source Codes (continued)

Codes Sources

- 17 U.S. Department of Energy, Energy Information Administration, October 1991, Inventory of Power Plants in the United States 1990, U.S. Department of Energy, 405 p. (U.S. Department of Energy, Energy Information Administration Forms: EIA 759 and EIA 767. [Power plants of a specified size must complete a variety of forms and surveys in compliance with federal regulations.])
- 18 U.S. Geological Survey, July 1975, Mineral and Water Resources of South Dakota.
- 19 Wyoming State Mine Inspector's Office, 1990, Annual Report. Also, communication with Arnold Hannum, Mine Inspector.
- **20 Wyoming Mining Association, 1991, Statistical Information on the Powder River Basin Coal Mines 1991.
- 21 Michie, Troy W., 1988, 1986 Production and Injection Statistics for Continental United States Appendix D, Michie and Associates, Inc., New Orleans, 17 p.
- 22 North Dakota Lignite Council.
- 23 North Dakota State Health Department, Division of Waste Management.
- More Information is Needed.
- NA Not Applicable.
- ** Proprietary sources, used to confirm information in selected areas.

A.2

NGPCOMP Database Status (6-30-92) *

	MT	ND	SD	WY
Production				
AGV	X	X	X	X
AGW	X	X	X	X
CM	X	X	X	X
DM	X	X	X	X
MP	X	X	X	X
NAGV	X	X	X	X
NAGW	X	X	X	X
OW	X	X	X	*
TCP	X	X	X	X
TGP	X	X	X	X
TGPW	X	X	X	X
TOP	X	X	X	*
Facilities				
BCD	X	X	NA	X
BSD	X	X	NA	X
CS	X	X	X	X
GPP	X	X	NA	X
IO	X	NA	NA	X
MM	X	X	NA	X
OREF	X	X	NA	X
PIPEL	--	--	--	--
POWP	X	X	X	X
PPTC	X	X	NA	X
PPTTP	X	X	NA	X
PS	--	--	--	--
TGC	X	X	X	X
TWG	X	NA	NA	X
USF	X	NA	NA	X
USSF	X	NA	NA	X
Class II				
AMP	X	X	X	--
DC	--	--	--	--
EORM	X	X	X	X
NAWP	X	X	X	--
SMDW	X	X	X	X
TCII	X	X	X	X
TWP	X	X	X	X

* Resources/Reserves, waste generation and management, used in marketing/consumption and in progress.

X 1990 data.

-- Information requisition ongoing.

NA Not applicable.

Abbreviation Key

Production Information

AGV	Associated Gas Production Volume (Mcf)
AGW	Associated Gas Wells
CM	Coal Mines
DM	Dedicated Mines (Where all production goes to one plant)
MP	Mixed Production (Where production is split with more than one plant, all of which are located "a few miles away")
NAGV	Non-Associated Gas Production Volume (Mcf)
NAGW	Non-Associated Gas Wells
OW	Oil Wells
TCP	Total Coal Production (Short Tons)
TGP	Total Gas Production (Mcf)
TGPW	Total Gas Producing Wells
TOP	Total Oil Production (Barrels)

Facility Information

BCD	Barrels per Calendar Day (Maximum number of barrels of input for a twenty-four hour period after making allowances for limitations, which include: environmental concerns, scheduled and unscheduled downtime, types and grades of input and expected output, and the capability of the downstream receiving facility)
BSD	Barrels per Stream Day (Amount of volume which can be processed at full capacity with optimum crude and product slate conditions)
CS	Compressor Stations
GPP	Gas Processing Plants
IO	Input and/or Output Well Total
MM	Mine-Mouth Generating Station
OREF	Oil Refineries
PIPEL	Oil, Gas and/or Product Pipelines
POWP	Power Plants (Generating Stations)
PPTC	Processing Plant Total Capacity (Mcf/d)
PPTTP	Processing Plant Total Through-Put (Mcf/d)
PS	Pump Stations
TGC	Total Gross Capacity (MW)
TWG	Total Working Gas (Mcf)
USF	Underground Gas Storage Facilities
USSF	Underground Gas Storage (Shared) Facilities (Reservoir is split between counties)

Class II Information

AWP	Produced Water Associated With Oil (Barrels)
DC	Direct Cost (Dollars/Barrel)
EORW	Enhanced Oil Recovery Wells
NAWP	Produced Water Associated With Gas (Non-Associated)
SWDW	Salt Water Disposal Wells
TCII	Total Class II Wells (SWDW + EORW)
TWP	Total Water Production
TOPQUAD	Total Oil Produced BTU. (In future BTU may be converted to quadrillion BTU.)

TGPQUAD	Total Gas Produced BTU. (In future BTU may be converted to quadrillion BTU.)
TCPQUAD	Total Coal Produced BTU. (In future BTU may be converted to quadrillion BTU.)
TQUAD	Total Calculated BTU. (In future BTU may be converted to quadrillion BTU.)
C1	Code for determining dominant hydrocarbon: 0 = No Production, 1 = Gas dominant, 2 = Oil dominant.
C2	Code for determining dominant fossil fuel type, hydrocarbon or coal: 0 = No Production, 2 = Gas and Oil Dominant, 3 = Coal Dominant.
OIL + GAS	Oil and Gas BTU Combined Total.

A.3

NGPCOMP Database Printout

ENERGY POLICY DATA BASE
PRODUCTION INFORMATION
PROVINCE TOTALS

COUNTY	OW	TOP	TGP	TGPW	NAGW	NAGV	AGW	AGV	CM	DM	MP	TCP
<u>Big Horn</u>												
Big Horn	521	3708732.00	4784767	345	42	3358720	303	1426047	0	0		0
Park	983	16601764.00	15850325	65	64	4945785	1	10904540	0	0		0
Washakie	304	1893117.00	3887170	283	20	2744834	263	1142336	0	0		0
Hot Springs	1035	6245586.00	452833	7	6	202819	1	250014	1	0		101961
Carbon	75	725196.00	1537591	94	37	993914	57	543677	0			0
Sum	2918	29174395.00	26512686	794	169	12246072	625	14266614	1	0		101961
<u>Central Montana Uplift</u>												
Treasure	0	0.00			0				0			
Musselshell	118	555198.00			0				1	0		14307
Fergus	0	0.00			0				0			
Golden Valley	1	1774.00			0				0			
Rosebud	114	675191.00	0	0	0	0	0	0	2	1	1	16403749
Sweet Grass	0	0.00			0				0			
Wheatland	0	0.00			0				0			
Blaine	76	312115.00	3618900	208	208	3618900	0	0	0			0
Petroleum	50	80786.00	0	0	0	0	0	0	0			
Stillwater	0	0.00			0				0			
Yellowstone	36	45944.00			0				0			
Sum	395	1671008.00	3618900	208	208	3618900	0	0	3	1	1	16418056
<u>Central Western Overthrust</u>												
Lincoln	894	659387.00	43843105	343	343	54066658	0	0	2	1		4735548
Uinta	188	8307628.00	216148558	147	145	92739873	2	123408685	0	0		0
Sum	1082	8967015.00	259991663	490	488	146806531	2	123408685	2	1		4735548
<u>Chadron arch</u>												
Shannon									0			
Sum									0			

COUNTY	OW	TOP	TGP	TGPW	NAGW	NAGV	AGW	AGV	CM	DM	MP	TCP
<u>Denver</u>												
Goshen	7	7120.00	3230	0	0	0	0	0	0	0	0	0
Laramie	107	539924.00	246864	0	0	0	0	0	0	0	0	0
Platte		0.00	0	0	0	0	0	0	0	0	0	0
Sum	114	547044.00	250094	0	0	0	0	0	0	0	0	0
<u>Green River</u>												
Sublette	286	1020927.00	248522448	714	713	266710706	1	0	0	0		0
Carbon	472	2509905.00	50818622	387	275	43097359	112	7721263	4	0		4511202
Albany	37	92928.00	24190	2	2	24190	0	0	0	0		0
Sweetwater	790	8977924.00	174442546	8354	858	147490792	7496	26951754	4	2	1	11936525
Sum	1585	12601684.00	473807806	9457	1848	457323047	7609	34673017	8	2	1	16447727
<u>Montana Folded Belt Province</u>												
Silver Bow	0	0.00			0					0		
Ravalli	0	0.00			0					0		
Gallatin	0	0.00			0					0		
Lake	0	0.00			0					0		
Park	0	0.00			0					0		
Meagher	0	0.00			0					0		
Beaverhead										0		
Madison	0	0.00			0					0		
Mineral	0	0.00			0					0		
Missoula	0	0.00			0					0		
Broadwater	0	0.00								0		0
Deer Lodge	0	0.00			0					0		
Jefferson	0	0.00			0					0		
Powell	0	0.00			0					0		
Lincoln	0	0.00			0					0		
Sanders	0	0.00			0					0		
Granite	0	0.00			0					0		
Sum	0	0.00			0					0		0
<u>North Western Overthrust</u>												
Lewis and Clark	0	0.00			0					0		
Flathead	0	0.00			0					0		
Sum	0	0.00			0					0		

COUNTY	OW	TOP	TGP	TGPW	NAGW	NAGV	AGW	AGV	CH	DM	MP	TCP
<u>Powder River</u>												
Big Horn	41	71402.00	0			0	0	0	3	0		20803203
Converse	1366	4229743.00	27064559	703	48	13616427	655	13448132	2	1		7890660
Sheridan	14	117389.00	17631	0	0	0	0	0	1	0		134104
Weston	1323	1597304.00	2275512	940	5	114195	935	2161317	0	0		0
Campbell	2304	26682965.00	22225586	1334	178	5557250	1156	16668336	17	1		154695691
Johnson	395	2616153.00	1488939	267	7	19429	260	1469510	0	0		0
Crook	574	5429359.00	101429	2	1	3662	1	97767	0	0		0
Niobrara	366	999493.00	1041866	127	4	27692	123	1014174	0	0		0
Custer	0	0.00	0			0	0	0	0			
Carter	0	0.00	0			0	0	0	0			
Powder River	79	485881.00	0	0	0	0	0	0	0			
Sum	6462	42229689.00	54215522	3373	243	19338655	3130	34859236	23	2		183523658
<u>Sioux Uplift</u>												
Jerauld									0			
Bennett									0			
Turner									0			
McCook									0			
Brookings									0			
Miner									0			
Moody									0			
Marshall									0			
Lincoln									0			
Lake									0			
Hamlin									0			
Faulk									0			
Gregory									0			
Davison									0			
Brule									0			
Tripp									0			
Bon Homme									0			
Spink									0			
Lyman									0			
Day									0			
Jackson									0			
Hanson									0			
Clark									0			
Beadle									0			
Deuel									0			
Clay									0			
Mellette									0			

COUNTY	OW	TOP	TGP	TGPW	NAGW	NAGV	AGW	AGV	CM	DM	MP	TCP
<u>Sioux Uplift</u>												
Roberts									0			
Todd									0			
Sanborn									0			
Codington									0			
Buffalo									0			
Union									0			
Minnehaha									0			
Yankton									0			
Edmunds									0			
Kingsbury									0			
Hyde									0			
Brown									0			
Charles Mix									0			
Douglas									0			
Aurora									0			
Grant									0			
Hutchinson									0			
Hand									0			
Sum									0			
<u>Sweetgrass Arch</u>												
Pondera	337	274685.00	0	0	0	0	0	0	0			
Glacier	690	1035054.00	952764	360	272	658874	88	293890	0			
Liberty	116	182030.00	1667629	250	164	1588629	86	79000	0			
Teton	145	104823.00	0	0	0	0	0	0	0			
Hill	4	1052.00	6225831	172	172	6225831	0	0	0			
Chouteau	0	0.00	0	45	45	791847	0	0	0			0
Cascade	0	0.00	0			0	0	0	0			
Toole	1192	600331.00	7195385	1748	656	6956935	1092	238450	0			
Judith Basin	0	0.00	0	0	0	0	0	0	0			
Sum	2484	2197975.00	16041609	2575	1309	16222116	1266	611340	0			0
<u>Williston Basin</u>												
Renville	320	1683244.00	525690		0	0		525690	0	0		0
Valley	48	275700.00	0	0	0	0	0	0	0			
Ward	29	221722.00	98765		0	0		98765	0			0
Ziebach									0			
Hughes									0			
Perkins									0			
Mercer	0	0.00	0						4	2	2	16608927
Dunn	96	1797760.00	3640495	3	3	3640495	0		0			

COUNTY	OW	TOP	TGP	TGPW	NAGW	NAGV	AGW	AGV	CM	DM	MP	TCP
<u>Williston Basin</u>												
Towner									0			
Rolette									0			
Sheridan									0			
Phillips	0	0.00	6484231	871	871	6484231	0	0	0			
Daniels	3	286833.00	0			0	0	0	0			0
Sheridan	214	2088558.00	1414665	212	0	0	212	1414665	0			
Barnes			0						0	0		
McKenzie	718	9957526.00	25898397	40	40	7404989	0	18493408	0			
Burleigh	0	0.00	0	0	0	0	0	0	0			0
Williams	393	4788557.00	11992363	13	13	11992363	0		1	1		10892
Slope	2	18106.00	22776		0	0		22776	0			
Garfield	17	47923.00	0	0	0	0	0	0	0			
Grant									0			
Steele									0			
Bottineau	563	2370365.00	261706		0				0			
Corson									0			
Richland	337	3390904.00	3558729	341	0	0	341	3558729	1			234010
Dewey	1	5456.00	0						0			0
Campbell									0			
Logan									0			
Dickey			0						0			
Golden Valley	38	494554.00	293106		0	0		293106	0			
Pembina									0			
Prairie	14	168072.00	0	0	0	0	0	0	0			
Kidder									0			
Foster									0			
Cavalier			0						0			
Oliver	0	0.00	0						1	1		4086938
Butte									0			
La Moure									0			
Meade									0			
Stark	59	827105.00	470080	1	1	470080	0		1	1		164813
McPherson									0			
Grand Forks									0			
Sioux									0			
Benson			0						0	0		
Lawrence									0			
Potter									0			
Wells									0			
Sully									0			
Billings	488	8510968.00	10685977	1			1	10685977	0			

COUNTY	OW	TOP	TGP	TGPW	NAGW	NAGV	AGW	AGV	CM	DM	MP	TCP
<u>Williston Basin</u>												
Walworth										0		
Stanley										0		
Fallon	411	5386037.00	1737991	484	86	275428	398	1462563	0			
McCone	20	54438.00	0	0	0	0	0	0	0			
McIntosh										0		
Ramsey										0		
Burke	323	787508.00	2748116					2748116	0			
Hettinger	0	0.00	0						0			
Emmons	0	0.00	0						0			
Adams			0						1	0		
Wibaux	77	1026856.00	0	0	0	0	0	0	0			
Mountrail	79	1389941.00	1330514		0	0		1330514	0			0
Stutsman									0			
Griggs									0			
Roosevelt	176	1395935.00	707666	78	1	13456	77	694210				
Custer	1	6557.00	0						0			0
Bowman	103	1300373.00	1196574	62	62	1196574			1	1		2054823
McHenry	20	51350.00	531		0	0		531	0			
Divide	78	1190506.00	3760675					3760675	0			
Jones									0			
Pierce									0			
Sargent									0			
Traill									0			
Eddy									0			
Dawson	39	300690.00	0	0	0	0	0	0	0			
Cass			0						0			
Richland									0			
Morton	0	0.00	0						0			
Haakon									0			
Ransom									0			
Walsh									0			
Nelson									0			
Fall River	24	224114.00	159596		0	0		159596	0			0
Harding	129	1426781.00	479232	54	54	479232	0	0	0			0
Pennington									0			
McLean	25	505693.00	311199		0	0		311199	1	1		6668109
Sum	4845	51980132.00	77779074	2160	1131	31956848	1029	45560520	11	7	2	29828512

COUNTY	OW	TOP	TGP	TGPW	NAGW	NAGV	AGW	AGV	CM	DM	MP	TCP
<u>Wind River</u>												
Natrona	2269	7856613.00	16377988	2087	63	7679801	2024	8698137	0	0		0
Fremont	887	3903670.00	54095254	310	234	53480484	76	614770	0	0		0
Sum	3156	11760283.00	70473242	2397	297	61160285	2100	9312907	0	0		0
<u>Yellowstone Province</u>												
Teton		0.00	0						0	0		0
Yellowstone	0	0.00			0				0			
National Park												
Sum	0	0.00	0		0				0	0		0
<u>Totals:</u>												
Sum	23041	161129225.00	982690596	21454	5693	748672454	15761	262692319	48	13	4	251055462

ENERGY POLICY DATA BASE
PRODUCED FOSSIL FUEL BTU INFORMATION
PROVINCE TOTALS

COUNTY	TOPOUAD	TGPOUAD	TCPOUAD	TQUAD	C1	C2	OIL + GAS
<u>Big Horn</u>							
Big Horn	19140766	4784767	0	23925533	2	2	23925533
Park	85681704	15850325	0	101532029	2	2	101532029
Washakie	9770377	3887170	0	13657547	2	2	13657547
Hot Springs	32233469	452833	1784318	34470620	2	2	32686302
Carbon	<u>3742737</u>	<u>1537591</u>	<u>0</u>	<u>5280328</u>	<u>2</u>	<u>2</u>	<u>5280328</u>
Sum	150569053	26512686	1784318	178866057	10	10	177081739
<u>Central Montana Uplift</u>							
Treasure	0	0	0	0	0	0	0
Musselshell	2865377	0	250373	3115750	2	2	2865377
Fergus	0	0	0	0	0	0	0
Golden Valley	9156	0	0	9156	2	2	9156
Rosebud	3484661	0	287065608	290550269	2	3	3484661
Sweet Grass	0	0	0	0	0	0	0
Wheatland	0	0	0	0	0	0	0
Blaine	1610826	3618900	0	5229726	1	2	5229726
Petroleum	416937	0	0	416937	2	2	416937
Stillwater	0	0	0	0	0	0	0
Yellowstone	<u>237117</u>	<u>0</u>	<u>0</u>	<u>237117</u>	<u>2</u>	<u>2</u>	<u>237117</u>
Sum	8624074	3618900	287315981	299558955	11	13	12242974
<u>Central Western Overthrust</u>							
Lincoln	3403096	43843105	82872090	130118291	1	3	47246201
Uinta	<u>42875668</u>	<u>216148558</u>	<u>0</u>	<u>259024226</u>	<u>1</u>	<u>2</u>	<u>259024226</u>
Sum	46278764	259991663	82872090	389142517	2	5	306270427
<u>Chadron arch</u>							
Shannon			<u>0</u>		<u>0</u>	<u>0</u>	
Sum			0		0	0	

COUNTY	TOPOUAD	TGPOUAD	TCPOUAD	TOUAD	C1	C2	OIL + GAS
<u>Denver</u>							
Goshen	36746	3230	0	39976	2	2	39976
Laramie	2786548	246864	0	3033412	2	2	3033412
Platte	0	0	0	0	0	0	0
Sum	2823294	250094	0	3073388	4	4	3073388
<u>Green River</u>							
Sublette	5269004	248522448	0	253791452	1	2	253791452
Carbon	12953620	50818622	89806455	153578697	1	3	63772242
Albany	479601	24190	0	503791	2	2	503791
Sweetwater	46335066	174442546	210056605	430834217	1	2	220777612
Sum	65037291	473807806	299863060	838708157	5	9	538845097
<u>Montana Folded Belt Province</u>							
Silver Bow	0	0	0	0	0	0	0
Ravalli	0	0	0	0	0	0	0
Gallatin	0	0	0	0	0	0	0
Lake	0	0	0	0	0	0	0
Park	0	0	0	0	0	0	0
Meagher	0	0	0	0	0	0	0
Beaverhead			0		0	0	
Madison	0	0	0	0	0	0	0
Mineral	0	0	0	0	0	0	0
Missoula	0	0	0	0	0	0	0
Broadwater	0	0	0	0	0	0	0
Deer Lodge	0	0	0	0	0	0	0
Jefferson	0	0	0	0	0	0	0
Powell	0	0	0	0	0	0	0
Lincoln	0	0	0	0	0	0	0
Sanders	0	0	0	0	0	0	0
Granite	0	0	0	0	0	0	0
Sum	0	0	0	0	0	0	0
<u>North Western Overthrust</u>							
Lewis and Clark	0	0	0	0	0	0	0
Flathead	0	0	0	0	0	0	0
Sum	0	0	0	0	0	0	0

COUNTY	TOPOUAD	TGPOUAD	TCPOUAD	TOUAD	C1	C2	OIL + GAS
<u>Powder River</u>							
Big Horn	368506	0	364056053	364424559	2	3	368506
Converse	21829704	27064559	138086550	186980813	1	3	48894263
Sheridan	605845	17631	2346820	2970296	2	3	623476
Weston	8243686	2275512	0	10519198	2	2	10519198
Campbell	137710782	22225586	2707174593	2867110961	2	3	159936368
Johnson	13501966	1488939	0	14990905	2	2	14990905
Crook	28020922	101429	0	28122351	2	2	28122351
Niobrara	5158383	1041866	0	6200249	2	2	6200249
Custer	0	0	0	0	0	0	0
Carter	0	0	0	0	0	0	0
Powder River	2507632	0	0	2507632	2	2	2507632
Sum	217947426	54215522	3211664016	3483826964	17	22	272162948
<u>Sioux Uplift</u>							
Jerauld			0		0	0	
Bennett			0		0	0	
Turner			0		0	0	
McCook			0		0	0	
Brookings			0		0	0	
Miner			0		0	0	
Moody			0		0	0	
Marshall			0		0	0	
Lincoln			0		0	0	
Lake			0		0	0	
Hamlin			0		0	0	
Faulk			0		0	0	
Gregory			0		0	0	
Davison			0		0	0	
Brule			0		0	0	
Tripp			0		0	0	
Bon Homme			0		0	0	
Spink			0		0	0	
Lyman			0		0	0	
Day			0		0	0	
Jackson			0		0	0	
Hanson			0		0	0	
Clark			0		0	0	
Beadle			0		0	0	
Deuel			0		0	0	
Clay			0		0	0	
Mellette			0		0	0	

COUNTY	TOPOUAD	TGPOUAD	TCPOUAD	TOUAD	C1	C2	OIL + GAS
<u>Sioux Uplift</u>							
Roberts			0		0	0	
Todd			0		0	0	
Sanborn			0		0	0	
Codington			0		0	0	
Buffalo			0		0	0	
Union			0		0	0	
Minnehaha			0		0	0	
Yankton			0		0	0	
Edmunds			0		0	0	
Kingsbury			0		0	0	
Hyde			0		0	0	
Brown			0		0	0	
Charles Mix			0		0	0	
Douglas			0		0	0	
Aurora			0		0	0	
Grant			0		0	0	
Hutchinson			0		0	0	
Hand			0		0	0	
Sum			0		0	0	
<u>Sweetgrass Arch</u>							
Pondera	1417649	498397	0	1916046	2	2	1916046
Glacier	5341914	952764	0	6294678	2	2	6294678
Liberty	939457	1667629	0	2607086	1	2	2607086
Teton	540992	0	0	540992	2	2	540992
Hill	5429	6225831	0	6231260	1	2	6231260
Chouteau	0	791847	0	791847	1	2	791847
Cascade	0	0	0	0	0	0	0
Toole	3098308	7195385	0	10293693	1	2	10293693
Judith Basin	0	0	0	0	0	0	0
Sum	11343749	17331853	0	28675602	10	14	28675602
<u>Williston Basin</u>							
Renville	8687222	525690	0	9212912	2	2	9212912
Valley	1422888	0	0	1422888	2	2	1422888
Ward	1144307	98765	0	1243072	2	2	1243072
Ziebach			0		0	0	
Hughes			0		0	0	
Perkins			0		0	0	
Mercer	0	0	209272480	209272480	0	3	0
Dunn	9278239	3640495	0	12918734	2	2	12918734

COUNTY	TOPOUAD	TGPOUAD	TCPOUAD	TOUAD	C1 C2	OIL + GAS
<u>Williston Basin</u>						
Towner			0		0 0	
Rolette			0		0 0	
Sheridan			0		0 0	
Phillips	0	6484231	0	6484231	1 2	6484231
Daniels	1480345	0	0	1480345	2 2	1480345
Sheridan	10779048	1414665	0	12193713	2 2	12193713
Barnes		0	0		0 0	
McKenzie	51390792	25898397	0	77289189	2 2	77289189
Burleigh	0	0	0	0	0 0 0	0
Williams	24713743	11992363	137239	36843345	2 2	36706106
Slope	93445	22776	0	116221	2 2	116221
Garfield	247331	0	0	247331	2 2	247331
Grant			0		0 0	
Steele			0		0 0	
Bottineau	12233454	261706	0	12495160	2 2	12495160
Corson			0		0 0	
Richland	17500456	3558729	2948526	24007711	2 2	21059185
Dewey	28158	0	0	28158	2 2	28158
Campbell			0		0 0	
Logan			0		0 0	
Dickey		0	0		0 0	
Golden Valley	2552393	293106	0	2845499	2 2	2845499
Pembina			0		0 0	
Prairie	867420	0	0	867420	2 2	867420
Kidder			0		0 0	
Foster			0		0 0	
Cavalier		0	0		0 0	
Oliver	0	0	51495419	51495419	0 3	0
Butte			0		0 0	
La Moure			0		0 0	
Meade			0		0 0	
Stark	4268689	470080	207664344	212403113	2 3	4738769
McPherson			0		0 0	
Grand Forks			0		0 0	
Sioux			0		0 0	
Benson		0	0		0 0	
Lawrence			0		0 0	
Potter			0		0 0	
Wells			0		0 0	
Sully			0		0 0	
Billings	43925106	10685977	0	54611083	2 2	54611083

COUNTY	TOPOUAD	TGPOUAD	TCPOUAD	TOUAD	C1 C2	OIL + GAS
<u>Williston Basin</u>						
Walworth			0		0 0	
Stanley			0		0 0	
Fallon	27797337	1737991	0	29535328	2 2	29535328
McCone	280955	0	0	280955	2 2	280955
McIntosh			0		0 0	
Ramsey			0		0 0	
Burke	4064329	2748116	0	6812445	2 2	6812445
Hettinger	0	0	0	0 0 0		0
Emmons	0	0	0	0 0 0		0
Adams		0	0		0 0	
Wibaux	5299604	0	0	5299604	2 2	5299604
Mountrail	7173486	1330514	0	8504000	2 2	8504000
Stutsman			0		0 0	
Griggs			0		0 0	
Roosevelt	7204421	707666	0	7912087	2 2	7912087
Custer	33841	0	0	33841	2 2	33841
Bowman	6711225	1196574	25890770	33798569	2 3	7907799
McHenry	265017	531	0	265548	2 2	265548
Divide	6144201	3760675	0	9904876	2 2	9904876
Jones			0		0 0	
Pierce			0		0 0	
Sargent			0		0 0	
Traill			0		0 0	
Eddy			0		0 0	
Dawson	1551861	87917	0	1639778	2 2	1639778
Cass		0	0		0 0	
Richland			0		0 0	
Morton	0	0	0	0 0 0		0
Haakon			0		0 0	
Ransom			0		0 0	
Walsh			0		0 0	
Nelson			0		0 0	
Fall River	1156652	159596	0	1316248	2 2	1316248
Harding	7363617	479232	0	7842849	2 2	7842849
Pennington			0		0 0	
McLean	2609882	311199	84018173	86939254	2 3	2921081
Sum	268269464	77866991	581426951	927563406	63 73	346136455

COUNTY	TOPOUAD	TGPOUAD	TCPOUAD	TOUAD	C1	C2	OIL + GAS
<u>Wind River</u>							
Natrona	40547980	16377988	0	56925968	2	2	56925968
Fremont	<u>20146841</u>	<u>54095254</u>	<u>0</u>	<u>74242095</u>	<u>1</u>	<u>2</u>	<u>74242095</u>
Sum	60694821	70473242	0	131168063	3	4	131168063
<u>Yellowstone Province</u>							
Teton	0	0	0	0	0	0	0
Yellowstone	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>
National Park							
Sum	0	0	0	0	0	0	0
Totals:							
Sum	831587936	984068757	4464926416	6280583109	**	**	1815656693

ENERGY POLICY DATA BASE
FACILITY INFORMATION
PROVINCE TOTALS

COUNTY	POWP	MM	TGC	OREF	BCD	BSD	PS	GPP	PPTC	PPTTP	CS	USF	USSF	IO	TWG	PIPEL
<u>PROVINCE: Big Horn</u>																
Big Horn				0				0			2	0				
Park				0				3	38500	20200	5	1		4	32235000	
Washakie				0				1	15000	12900	1	0				
Hot Springs				0				0			1	0				
Carbon								0				1		9	10567000	
Sum				0				4	53500	33100	9	2		13	42802000	
<u>PROVINCE: Central Montana Uplift</u>																
Treasure																
Musselshell																
Fergus																
Golden Valley																
Rosebud	2	2		2414												
Sweet Grass																
Wheatland																
Blaine				0				0			3	1 T		7	4423000	
Petroleum																
Stillwater											2					
Yellowstone	1	0		160	3	131900										
Sum	3	2		2574	3	131900		0			5	1		7	4423000	
<u>PROVINCE: Central Western Overthrust</u>																
Lincoln	1	1		700	0			3	1005000	801100	3	0				
Uinta					0			7	1375000	1192600	1	1		9	1109000	
Sum	1	1		700	0			10	2380000	1993700	4	1		9	1109000	
<u>PROVINCE: Chadron arch</u>																
Shannon																
Sum																

COUNTY	POWP	MM	TGC	OREF	BCD	BSD	PS	GPP	PPTC	PPTTP	CS	USE	USSE	IO	TWG	PIPEL
<u>PROVINCE: Denver</u>																
Goshen												1				
Laramie				1	36100	38000		0				0	0			
Platte	1	0	1800	0				0	0			1	0			
Sum	1	0	1800	1	36100	38000		0	0			2	0			
<u>PROVINCE: Green River</u>																
Sublette				0				0				1	0			
Carbon				1	54000	55000		2	200500	216200		6	3	6	5107000	
Albany				0				0				1	0			
Sweetwater	1	1	2080	0				5	330000	204000		9	0			
Sum	1	1	2080	1	54000	55000		7	530500	420200		17	3	6	5107000	
<u>PROVINCE: Montana Folded Belt Province</u>																
Silver Bow												1				
Ravalli																
Gallatin																
Lake																
Park																
Meagher																
Beaverhead																
Madison																
Mineral																
Missoula																
Broadwater																
Deer Lodge																
Jefferson												1				
Powell												1				
Lincoln																
Sanders																
Granite																
Sum												3				
<u>PROVINCE: North Western Overthrust</u>																
Lewis and Clark												1				
Flathead																
Sum												1				

COUNTY	POW	MM	TGC	OREF	BCD	BSD	PS	GPP	PPTC	PPTTP	CS	USF	USSF	IO	TWG	PIPEL
<u>PROVINCE: Powder River</u>																
Big Horn				0				0					0			
Converse	1	1	750	0				5	164000	90000	3	0				
Sheridan																
Weston	1	0	33	1	12500	13500		1	5000	3000	0	0				
Campbell	2	2	382	0				6	147500	57600	2	0				
Johnson				0				0			1	1		5	2180000	
Crook				0				0	0	0	0	0				
Niobrara				0				0			0	0				
Custer											2					
Carter				0				0				0				
Powder River																
Sum	4	3	1165	1	12500	13500		12	316500	150600	8	1		5	2180000	

PROVINCE: Sioux Uplift

Jerauld
 Bennett
 Turner
 McCook
 Crookings
 Miner
 Moody
 Marshall
 Lincoln
 Lake
 Hamlin
 Faulk
 Gregory
 Davison
 Brule
 Tripp
 Bon Homme
 Spink
 Lyman
 Day
 Jackson
 Hanson
 Clark
 Beadle
 Deuel
 Clay
 Mellette

COUNTY	POWP	MM	TGC	OREF	BCD	BSD	PS	GPP	PPTC	PPTTP	CS	USF	USSF	IO	TWG	PIPEL
<u>PROVINCE: Sioux Uplift</u>																
Roberts																
Todd																
Sanborn																
Codington																
Buffalo																
Union																
Minnehaha																
Yankton																
Edmunds																
Kingsbury																
Hyde																
Brown																
Charles Mix																
Douglas																
Aurora																
Grant		1		440												
Hutchinson																
Hand																
Sum		1		440												
<u>PROVINCE: Sweetgrass Arch</u>																
Pondera												1				
Glacier												1	1 T	16	8311000	
Liberty																
Teton												1				
Hill													1 T			
Chouteau												3				
Cascade					1	7000	7200									
Toole												2	2 T	3	1264000	
Judith Basin																
Sum					1	7000	7200					8	4	19	9575000	
<u>PROVINCE: Williston Basin</u>																
Renville					0			0				0	0			
Valley												2				
Ward					0			0				0	0			
Ziebach																
Hughes																
Perkins																
Mercer		5	4	2257	0			0				0	0			
Dunn					0			1		16900		1	0			

COUNTY	POWP	MM	TGC	OREF	BCD	BSD	PS	GPP	PPTC	PPTTP	CS	USF	USSF	IO	TWG	PIPEL
PROVINCE: Williston Basin																
Towner																
Rolette																
Sheridan																
Phillips																
Daniels																
Sheridan																
Barnes																
McKenzie				0				3	82000	55300		1	0			
Burleigh				0				0				1	0			
Williams				0				1	4000	2000		1	0			
Slope				0				0				0	0			
Garfield																
Grant																
Steele																
Bottineau				0				0				0	0			
Corson																
Richland	1	1		48				3	21000	6300						
Dewey				0				0				0	0			
Campbell																
Logan																
Dickey																
Golden Valley				0				0				0	0			
Pembina																
Prairie																
Kidder																
Foster																
Cavalier																
Oliver	1	1		734	0			0				0	0			
Butte																
La Moure																
Meade																
Stark				0				0				2	0			
McPherson																
Grand Forks																
Sioux																
Benson																
Lawrence	1			33												
Potter																
Wells																
Sully																
Billings				0				1	65000	27800		0	0			

COUNTY	POWP	MM	TGC	OREF	BCD	BSD	PS	GPP	PPTC	PPTTP	CS	USF	USSE	IO	TWG	PIPEL
PROVINCE: Williston Basin																
Walworth																
Stanley																
Fallon								3	4800	3600	3	1		182	195778000	
McCone											1					
McIntosh																
Ramsey																
Burke				0				1	11000	6300	0	0				
Hettinger				0				0			0	0				
Emmons				0				0			1	0				
Adams				0				0	0	0	0	0		0	0	
Wibaux								1								
Mountrail				0				0			0	0				
Stutsman																
Griggs																
Roosevelt																
Custer				0				0			0	0				
Bowman				0				1	3000	600	0	0				
McHenry				0				0			0	0				
Divide				0				0			0	0				
Jones																
Pierce																
Sargent																
Trall																
Eddy																
Dawson											1					
Cass																
Richland																
Morton	1		91	1	58000	60000		0			0	0				
Haakon																
Ransom																
Walsh																
Nelson																
Fall River				0				0			0	0				
Harding				0				0			1	0				
Pennington	1		22													
McLean	1	1	1130	0				0			0	0				
Sum	11	7	4315	1	58000	60000		15	190800	118800	15	1		182	195778000	

COUNTY	POWP	MM	TGC	OREF	BCD	BSD	PS	GPP	PPTC	PPTTP	CS	USF	USSE	IO	TWG	PIPEL
<u>PROVINCE: Wind River</u>																
Natrona				2	62000	65000		4	97000	56100	5	0				
Fremont				<u>0</u>				<u>3</u>	<u>109000</u>	<u>33300</u>	<u>6</u>	<u>1</u>		<u>1</u>	<u>494000</u>	
Sum				2	62000	65000		7	206000	89400	11	1		1	494000	
<u>PROVINCE: Yellowstone Province</u>																
Teton				0				0			0	0				
Yellowstone																
National Park																
Sum				0				0			0	0				
<u>Totals:</u>																
Sum	22	14	13074	10	361500	377200		55	3677300	2805800	83	14		242	261468000	

ENERGY POLICY DATA BASE
CLASS II INFORMATION
PROVINCE TOTALS

COUNTY	AWP	NAWP	TWP	SWDW	EORW	TCII	DC

Big Horn							
Big Horn			161123014	9	32	41.00	
Park			476402301	19	178	197.00	
Washakie			10693666	7	14	21.00	
Hot Springs			205568115	8	334	342.00	
Carbon	4995197.00	0.00	4995197	0	13	13.00	
Sum	4995197.00	0.00	858782293	43	571	614.00	
Central Montana Uplift							
Treasure							
Musselshell	11590705.00	0.00	11590705	5	29	34.00	
Fergus							
Golden Valley	24271.00	0.00	24271				
Rosebud	164976.00	0.00	16400976	5	41	46.00	
Sweet Grass							
Wheatland							
Blaine	701331.00	0.00	701331	1	4	5.00	
Petroleum	2505985.00	0.00	2505985	1	9	10.00	
Stillwater				0	0	0.00	
Yellowstone	746050.00	0.00	746050	1	0	1.00	
Sum	15733318.00	0.00	31969318	13	83	96.00	
Central Western Overthrust							
Lincoln			869167	1	0	1.00	0.00
Uinta			5469154	12	5	17.00	0.00
Sum			6338321	13	5	18.00	0.00
Chadron arch							
Shannon							
Sum							

COUNTY	AWP	NAWP	TWP	SWDW	EORW	TCII	DC

Denver							
Goshen			1255	0	0	0.00	
Laramie			1340261	1	6	7.00	
Platte				0	0	0.00	
Sum			1341516	1	6	7.00	
Green River							
Sublette			7318964	15	23	38.00	0.00
Carbon			30472759	5	7	12.00	0.00
Albany			2589160	1	4	5.00	
Sweetwater			62525430	7	102	109.00	0.00
Sum			102906313	28	136	164.00	0.00
Montana Folded Belt Province							
Silver Bow				0	0	0.00	
Ravalli							
Gallatin							
Lake							
Park							
Meagher							
Beaverhead							
Madison							
Mineral							
Missoula							
Broadwater							
Deer Lodge							
Jefferson				0	0	0.00	
Powell				0	0	0.00	
Lincoln							
Sanders							
Granite							
Sum				0	0	0.00	

COUNTY	AWP	NWP	TWP	SWDW	EORW	TCII	DC
North Western Overthrust							
Lewis and Clark				0	0	0.00	
Flathead							
Sum				0	0	0.00	
Powder River							
Big Horn	805944.00	0.00	805944	0	0	0.00	
Converse			9092532	15	41	56.00	0.00
Sheridan			1337745	2	8	10.00	
Weston			7272650	5	252	257.00	1.00
Campbell			83810388	86	398	484.00	0.00
Johnson			27329948	4	57	61.00	0.00
Crook			23996381	34	104	138.00	
Niobrara			7616068	2	4	6.00	1.00
Custer				0	0	0.00	
Carter				1	0	1.00	
Powder River	10932928.00	0.00	10932928	1	68	69.00	
Sum	11738872.00	0.00	172194584	150	932	1082.00	2.00
Sioux Uplift							
Jerauld							
Bennett							
Turner							
McCook							
Brookings							
Miner							
Moody							
Marshall							
Lincoln							
Lake							
Hamlin							
Faulk							
Gregory							
Davison							
Brule							
Tripp							
Bon Homme							
Spink							
Lyman							
Day							
Jackson							

COUNTY	AWP	NWP	TWP	SWW	EORW	TCII	DC

Sioux Uplift							
Hanson							
Clark							
Beadle							
Deuel							
Clay							
Mellette							
Roberts							
Todd							
Sanborn							
Codington							
Buffalo							
Union							
Minnehaha							
Yankton							
Edmunds							
Kingsbury							
Hyde							
Brown							
Charles Mix							
Douglas							
Aurora							
Grant							
Hutchinson							
Hand							
Sum							
Sweetgrass Arch							
Pondera	3835831.00	0.00	3835831	25	0	25.00	
Glacier	7710101.00	0.00	7710101	23	120	143.00	
Liberty	383689.00	0.00	383689	0	18	18.00	
Teton	1260732.00	0.00	1260732	1	1	2.00	
Hill	0.00			0	0	0.00	
Chouteau				0	0	0.00	
Cascade	0.00	0.00	0	0	0	0.00	
Toole	3677155.00	0.00	3677155	6	12	18.00	0.00
Judith Basin							

COUNTY	AWP	NAWP	TWP	SWDW	EORW	TCII	DC
Sum	16867508.00	0.00	16867508	55	151	206.00	0.00
Williston Basin							
Renville	6620078.00	0.00	6620078	37	4	41.00	
Valley	1179235.00	0.00	1179235	6	0	6.00	
Ward	765060.00		765060	6	0	6.00	
Ziebach							
Hughes							
Perkins							
Mercer				0	0	0.00	
Dunn	1811100.00	0.00	1811100	13	0	13.00	
Towner							
Rolette							
Sheridan							
Phillips				0	0	0.00	
Daniels	117303.00	0.00	117303	0	0	0.00	
Sheridan	11952223.00	0.00	11952223	28	22	50.00	0.00
Barnes							
McKenzie	17483462.00	0.00	17483462	45	61	106.00	
Burleigh	0.00	0.00	0	0	0	0.00	
Williams	11775820.00	0.00	11775820	31	57	88.00	
Slope	27213.00	0.00	27213	0	2	2.00	
Garfield	187703.00	0.00	187703	1	3	4.00	
Grant							
Steele							
Bottineau	18971994.00	0.00	18971994	54	49	103.00	
Corson							
Richland	5155200.00	0.00	5155200	18	3	21.00	0.00
Dewey				0	0	0.00	
Campbell							
Logan							
Dickey							
Golden Valley			1449318	8	0	8.00	
Pembina							
Prairie	980017.00	0.00	980017	0	3	3.00	
Kidder							
Foster							
Cavalier							
Oliver				0	0	0.00	
Butte							
La Moure							

COUNTY	AWP	NAWP	TWP	SWDW	EORW	TCII	DC
Williston Basin							
Meade							
Stark	5105420.00	0.00	5105420	6	34	40.00	
McPherson							
Grand Forks							
Sioux							
Benson							
Lawrence							
Potter							
Wells							
Sully							
Billings	16981520.00	0.00	16981520	40	38	78.00	
Walworth							
Stanley							
Fallon	18715191.00	0.00	18715191	10	148	158.00	0.00
McCone	888037.00	0.00	888037	3	0	3.00	
McIntosh							
Ramsey							
Burke	2088541.00	0.00	2088541	18	0	18.00	
Hettinger	0.00	0.00	0	1	0	1.00	
Emmons	1449318.00	0.00		0	0	0.00	
Adams							
Wibaux	6915424.00	0.00	6915424	2	20	22.00	
Mountrail	1445654.00	0.00	1445654	8	5	13.00	
Stutsman							
Griggs							
Roosevelt	12654832.00	0.00	12654832	25	0	25.00	0.00
Custer	7682.00			1	0	1.00	
Bowman	3849803.00	0.00	3849803	6	30	36.00	
McHenry	459331.00	0.00	459331	2	0	2.00	
Divide	1282665.00	0.00	1282665	8	2	10.00	
Jones							
Pierce							
Sargent							
Traill							
Eddy							
Dawson	1179263.00	0.00	1179263	6	3	9.00	0.00
Cass							
Richland							
Morton				0	0	0.00	
Haakon							

COUNTY	AWP	NAWP	TWP	SWDW	EORW	TCII	DC
Williston Basin							
Ransom							
Walsh							
Nelson							
Fall River	1522811.00			0	2	2.00	
Harding	1080221.00	368.00	1080589	6	4	10.00	
Pennington							
McLean	<u>148217.00</u>	<u>0.00</u>	<u>148217</u>	<u>1</u>	<u>0</u>	<u>1.00</u>	
Sum	152800338.00	368.00	151270213	390	490	880.00	0.00
Wind River							
Natrona			443983308	18	1004	1022.00	
Fremont			<u>135159116</u>	<u>12</u>	<u>171</u>	<u>183.00</u>	
Sum			579142424	30	1175	1205.00	
Yellowstone Province							
Teton				0	0	0.00	
Yellowstone							
National Park							
Sum				0	0	0.00	
Totals:							
Sum	202135233.00	368.00	1920812490	723	3549	4272.00	2.00

A.4

Draft Maps from the **NGPCOMP** Database

A.5

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27. Total Electrical Generating Capacity by County

ENERGY POLICY STUDY AREA

ENERGY POLICY STUDY AREA: GEOLOGIC PROVINCES

ENERGY POLICY STUDY AREA: COUNTIES

ENERGY POLICY STUDY AREA: GEOLOGIC PROVINCES & COUNTIES

TOTAL FOSSIL FUEL BTU OUTPUT BY COUNTY

PRODUCED OIL BTU OUTPUT BY COUNTY

PRODUCED GAS BTU OUTPUT BY COUNTY

PRODUCED COAL BTU OUTPUT BY COUNTY

COAL VS GAS + OIL PRODUCTION

Dominant Production Type

- ☐ no production
- ☒ gas+oil production dominant
- ☐ coal production dominant

OIL VS GAS PRODUCTION BY COUNTY

TOTAL OIL PRODUCTION BY COUNTY

TOTAL GAS PRODUCTION BY COUNTY (ASSOCIATED AND NONASSOCIATED GAS)

NONASSOCIATED GAS PRODUCTION BY COUNTY

TOTAL PRODUCED WATER BY COUNTY

TOTAL COAL PRODUCTION BY COUNTY

OIL WELLS BY COUNTY

NONASSOCIATED GAS WELLS BY COUNTY

COAL MINES BY COUNTY

Coal mines

TOTAL CLASS II WELLS (EOR + SWD) BY COUNTY

SALT WATER DISPOSAL (SWD) WELLS BY COUNTY

ENHANCED OIL RECOVERY (EOR) WELLS BY COUNTY

COMPRESSOR STATIONS BY COUNTY

OIL REFINERIES BY COUNTY

GAS PROCESSING FACILITIES BY COUNTY

NATURAL GAS UNDERGROUND STORAGE FACILITIES BY COUNTY

COAL-FIRED ELECTRICAL PLANTS BY COUNTY

TOTAL ELECTRICAL GENERATING CAPACITY BY COUNTY

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORTFORM APPROVED
OMB NO. 1900-0127
Page 1 of 3

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Regional Energy Policy Program for the Northern Great Plains (2.3)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-86
		6. Completion Date 9-30-92

7. FY 91/92	8. Months or Quarters	1991												1992					
	Quarters	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN						
9. Cost Status	a. Dollars Expressed in Thousands	b. Dollar Scale																	
10. Cost Chart
Fund Source		Quarter				Cum. to Date	Tot. Plan												
		1st	2nd	3rd	4th														
DOE	P	15	15	15	16	150	150												
	A	11	10	17	10	137													
	P																		
	A																		
	P																		
	A																		
	P																		
	A																		
Total P		15	15	15	16	150	150												
Total A		11	10	17	10	137													
Variance		4	5	(2)	6	13													
P = Planned A = Actual		c. Cumulative Accrued Costs																	
Total Planned Costs for Program/Project		Planned																	
\$150		Actual																	
		Variance																	
				104			119			134			150						
				101			110			127			137						
				3			9			7			13						

11. Major Milestone Status	Units Planned	Units Complete
A. Information Management System	P	C
		1A 2A 2A 3A 4A
B. Information Acquisition, Evaluation, and Organization	P	C
		1A 2A 3A 4A 5A 6A 7A
C. Energy Resources	P	C
		1A 2A 3A 4A 5A 6A 7A
D. Production/Transportation	P	C
		1A 2A 3A 4A 5A 6A 7A
E. Energy Consumption	P	C
		1A 2A 3A 4A 5A 6A 7A
F. Technology	P	C
		1A 2A 3A 4A 5A 6A 7A
G. Government Policy	P	C
		1A 2A 3A 4A 5A 6A 7A
H. Environmental Status Reports	P	C
		1A 2A 3A 4A 5A 6A 7A

12. Remarks

Due to EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date

Wendy Day 7-10-92

14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Regional Energy Policy Program for the Northern Great Plains (2.3)		3. Reporting Period 4-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-6000				5. Program/Project Start Date 4-1-88	
				6. Completion Date 6-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Information Management System ¹				
a.1	Design of data management shell	12-91	12-91	Begin 3-92	
a.2	Obtain/link software	1-92	3-92		
a.3	Relating data sets	5-92			
a.4	Demonstration data base shell	6-92			
Task B	Information Acquisition, Evaluation, and Organization Annotated Bibliography Data Base				
b.1	Designation of subject areas	9-91	9-91		
	Subject area evaluation				
b.2	Coal	10-91	10-91		
b.3	Oil	11-91	11-91		
b.4	Gas	12-91	12-91		
b.5	Electricity	1-92	1-92		
b.6	Nonfossil energy	2-92	2-92		
b.7	Other	3-92	3-92		
b.8	Organizations Data Base	12-91	12-91		
Task C	Energy Resources Status of Resource Assessment ²				
c.1	Coal	12-91			
c.2	Oil and gas	1-92			
c.3	Nonfossil energy	2-92			
	Resource Data Base ³				
c.4	Coal	3-92			
c.5	Oil and gas	4-92			
c.6	Nonfossil energy	5-92			
Task D	Production/Transportation ³ Facility Data Base				
	Coal				
d.1	Mines	11-91	12-91		
d.2	Conversion facilities	12-91	12-91		
	Oil				
d.3	Refineries	4-92			
	Gas				
d.4	Processing and transportation	4-92			

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Regional Energy Policy Program for the Northern Great Plains (2.3)		3. Reporting Period 4-1-92 through 6-31-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 6-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
	Production Data Base ³				
d.5	Coal	3-92			
d.6	Oil and gas	4-92			
d.7	Nonfossil energy	5-92			
Task E	Energy Consumption ³				
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f.1	Low-rank coal conversion technologies data base	12-91	12-91		
Task G	Government Policy ²				
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g.2	North Dakota	3-92			
g.3	Montana	--			
g.4	Wyoming	--			
g.5	South Dakota	--			
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h.2	Clean Air Act	1-92			
h.3	Coal conversion waste management	2-92			
h.4	Surface mining and reclamation	3-92			
h.5	Leasing on federal lands	3-92			

¹ Hardware acquisition for Atlas® GIS was completed in May 1992; current focus on data entry and report and map output.

² In progress.

³ In progress as part of attribute file development for the GIS system under Task A (a.3).

2.4 Hot-Gas Cleanup

HOT-GAS CLEANUP

**Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992**

by

**Michael L. Jones, CESRI Director
Jay S. Haley, Research Engineer
John Hurley, Research Supervisor
Blazo Ljubicic, Research Engineer
Murali Ramanathan, Research Scientist**

**Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
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Technical Monitor: Richard A. Dennis

for

**U.S. Department of Energy
Morgantown Energy Technology Center
3610 Collins Ferry Road
P.O. Box 880, Mail Stop E02
Morgantown, WV 26507-0880**

July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

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HOT-GAS CLEANUP

1.0 INTRODUCTION

The U.S. Department of Energy (DOE) is promoting the development of coal-based advanced power systems under the direction of the Morgantown Energy Technology Center (METC). This activity covers a broad range of technologies involving combustion, gasification, and the integration of combustion and gasification technologies. The objective is to maximize cycle efficiencies to provide for a stable, secure, and environmentally sound energy future.

Specific combustion program areas include the development of heat engines such as direct coal-fired turbines and diesels and pressurized fluidized-bed combustion (PFBC). Gasification technology development includes mild gasification for coproducts and hydrogen and methane production for fuel cell applications. Integrated gasification combined cycle (IGCC) technology promotes high cycle efficiencies by combining coal gasification with direct product-gas firing in turbines. In all of these cases, hot-gas cleanup systems are required to achieve acceptable process performance and to meet current and future environmental emission standards.

2.0 GOALS AND OBJECTIVES

The goals of the hot-gas cleanup project at the Energy and Environmental Research Center (EERC) are to build and operate a hot-gas cleanup test loop in conjunction with various pilot-scale advanced systems currently in operation at the Center and to explore the various ash/alkali corrosion mechanisms for ceramic barrier filter materials and to determine the effects of various mitigation options. The mitigation options will focus primarily on gettering techniques. Eventually these techniques will be verified at the pilot scale using the hot-gas test loop.

The Center is currently operating the following pilot-scale fluidized-bed reactors:

- Fluidized-bed mild gasification reactor
- Fluidized-bed catalytic reactor for the production of hydrogen
- Pressurized fluidized-bed combustor

The Center is also planning to install and operate a transport reactor test unit (TRTU) to provide scaleup data for the hot-gas cleanup test facility in Wilsonville, Alabama.

3.0 PROJECT DESCRIPTION

The Energy and Environmental Research Center is currently involved in a number of research projects in both the combustion and gasification of coal and also in gas-stream cleanup. The fundamental gas-stream cleanup issues common to the various advanced concept systems are being investigated in this

project. Emphasis is being placed on particulate control techniques and on ash/alkali interactions with the filter materials.

In order to investigate particulate control methods, a test loop was constructed and inserted into the exhaust piping of the advanced concept reactors at the Center. The test loop provides a means of exposing various hot-gas cleanup systems to actual product gases from coal gasification and combustion using fluidized-bed reactors. Long-term effects on hot-gas cleanup systems can be studied economically by passively participating in the various research gasification and combustion runs. Filter efficiency, strength degradation, changes in permeability, and corrosion resistance are being investigated, as well as other pertinent issues such as cleaning techniques and temperature/pressure effects.

The Center has been involved in research related to ash/alkali interactions and slag behavior for many years. This expertise is being used in studying the effects of alkali interactions with filter media and possible mitigation options that may improve filter life. The global or overall objective in this phase of the project is the study of the thermodynamically equilibrated reaction mechanisms and mineral matter transformations in advanced coal combustion systems.

During this reporting period, bench-scale tests of kaolin as an entrained alkali getter in atmospheric and pressurized coal combustion conditions were performed. In addition, software was improved to permit a computer model study of other possible getters and getter concentrations.

The thermochemical equilibrium calculation package PHOEBE, developed at the EERC, was selected as the software tool to perform this study. After a careful review of the current state of development of PHOEBE, two major components of the package were identified as being critical to the applicability of the package to advanced coal combustion systems and in need of further development.

A framework for the requisite development was established. This framework was comprised of two tasks. The first was to address the enlargement of the database component of PHOEBE so that chemical species characteristic of advanced coal combustion systems would be well represented in the database. The second was set up to address the algorithmic aspects of the package so that the equilibrium computations would be pressure-dependent. (Since the system pressure is a critical operational parameter, sensitivity to variations in pressure is required of any equilibrium computation package used in this context.)

4.0 ACCOMPLISHMENTS

4.1 Particulate Control

A hot-gas cleanup test loop has been designed and constructed for use with each of the three reactors (Figure 1). The test loop was constructed using high-alloy metals with no refractory in order to minimize maintenance and to avoid ash/alkali/refractory interactions that may occur due to the high surface-to-volume ratio present in smaller-scale systems. The alloys used in construction were Haynes alloys HR-160 and 556, and 316H stainless steel. The

Figure 1. Hot-gas cleanup test loop.

piping used in the highest-temperature regions was HR-160 and 556. It is expected that these alloys will demonstrate good high-temperature corrosion characteristics under both oxidizing and reducing conditions. The test loop is designed to operate at temperatures up to 1650°F and pressures up to 150 psig. The system was designed in accordance with B31.3 piping codes. The test loop consists of a single inlet pipe which branches into three different flow paths. Each path is controlled by a high-temperature valve located as far downstream as possible in order to minimize thermal stresses in the valves. Two of the flow paths are identical and are used as filter element test bays, and the third branch is used as a bypass line. Filter elements can be installed in either or both test bays simultaneously. The filter modules are flange-mounted so that they may be replaced as necessary for different

filter types. The flanges used currently will permit operating conditions up to 1500°F and 150 psig. In order to achieve operating conditions up to 1650°F and 150 psig, further engineering is required to ensure that the flanged connection satisfies the criteria of the B31.3 piping code. The system will not be operated above 1500°F and 150 psig until this work has been completed. Gas flow rates through the various paths can be regulated by the downstream valves. The piping system is heated electrically using guard heaters. Pipe temperatures can be maintained at 1650°F continuously so that the process gas temperature can be raised or maintained as required in order to simulate the desired hot-gas conditions. The system has a heated backpulse system capable of delivering pressurized, heated, inert gas to the filter modules for cleaning purposes. The inlet piping to the test loop can be connected to a 100-lb/hr fluidized-bed gasifier or to other reactors being used for research at the Center. The TRTU is expected to be operational sometime in early 1993 and will be installed near the 100-lb/hr fluidized-bed reactor. The test loop will be connected to the TRTU when it is ready for operation.

To effectively use filter elements for a given application, many variables need to be considered, including system temperature, system pressure, initial clean pressure drop, total allowable pressure drop, system flow rate, etc. Any combination of these factors can affect the resulting filter efficiency.

Before a final parametric study was performed to define the characteristics of unsteady flow associated with the heated nitrogen backpulse system, research was conducted on the cleanup system. The goal was to determine backpulse operating range (minimum and maximum pulse duration) and to define solenoid valve operating policy that will maximize nitrogen backpulse cleaning efficiency.

Operating policy was specified by nitrogen pressure and backpulse duration. Three levels of nitrogen pressure were analyzed: 18, 37, and 60 psi. Pulse duration was controlled by a computer-controlled solenoid valve. Valve-opening duration was increased from 0.1 to 1 sec, with time increments of 0.1 sec; from 1 to 2 sec, with time increments of 0.25 sec; and from 2 to 3 sec, with time increments of 0.5 sec. Finally, the solenoid valve was opened for 90 sec, and nitrogen temperature versus time dependence was determined. For all tests, pressure and temperature at the points relevant to filter behavior over the observation periods were recorded and data stored in a computer.

Nitrogen pressure variation as a function of time and pulse duration is shown in Figures 2 through 4. For all three different initial pressure levels, minimum pressure reached was a strong function of pulse duration: the longer the pulse, the lower the minimum system pressure observed. Tests with the solenoid valve permanently open indicate that minimum pressure was reached in a maximum 8-sec period for all pressure levels (see Figures 5 through 7).

Backpulse gas temperature at the front of the filter for three different pressure levels is shown in Figures 8 through 10. Results indicate that pulse durations less than 2 sec were not long enough to ensure that the maximum temperature was reached. A higher initial pressure level resulted in a higher maximum gas temperature reached at the front of the filter. Infinite pulse tests showed that, once maximum temperature was reached, it remained constant as long as the solenoid valve was open (Figures 5 through 7).

Figure 2. Nitrogen pressure variation ($p_{\text{initial}} = 18$ psi).

Figure 3. Nitrogen pressure variation ($p_{\text{initial}} = 37$ psi).

Figure 4. Nitrogen pressure variation ($p_{initial} = 60$ psi).

Infinite Pulse

Valve Open at $t=2$ sec

Figure 5. Infinite pulse ($p_{initial} = 18$ psi).

Infinite Pulse

Figure 6. Infinite pulse ($p_{initial} = 37$ psi).

Infinite Pulse

Figure 7. Infinite pulse ($p_{initial} = 60$ psi).

Figure 8. Backpulse gas temperature in front of the filter ($p_{\text{initial}} = 18$ psi).

Figure 9. Backpulse gas temperature in front of the filter ($p_{\text{initial}} = 37$ psi).

Figure 10. Backpulse gas temperature in front of the filter ($p_{\text{initial}} = 60$ psi).

Pressure wave intensity in front of the filter showed that both intensity and pulse duration are directly dependent on initial pressure level (see Figures 11 through 13). As expected, higher initial pressure resulted in a higher pressure wave intensity. The longer the solenoid valve was open, the longer the pulse duration that was involved.

A high-temperature, high-pressure, particle sampling system is being developed for use with the hot-gas cleanup test loop. This sampling system must meet the National Electrical Code (NEC) and B31.3 piping requirements as well as allowing sampling at the extreme operating conditions of the test loop. Aside from code-related issues, the particle sampling system currently in use is slow and cumbersome to use. A separate probe must be inserted to make flow measurements, then the particulate probe must be inserted to make dust-loading measurements. It takes approximately 45 to 60 minutes to collect one sample with the current configuration. While this system may be adequate for intermittent measurements on a temporary basis, it is inadequate for safe, reliable, long-term work. The particulate sampling system is being designed to sample at pressures up to 200 psi at a temperature of 1800°F under both oxidizing and reducing conditions. Table 1 shows the performance specifications for the sample system, and Figure 14 shows the sampling system. A sampling probe is inserted into the test loop, and a particulate sample is withdrawn isokinetically. The sample probe is considered to be disposable (based on wear). Different materials will be used for different operating conditions. The gas sample will pass through a series of cyclones and a borosilicate filter to remove all particulate matter, then through a quench train to remove any condensables, then through gas meters to determine flow. The probe and cyclone assembly will be electrically heated to maintain the gas temperature until it reaches the quench train.

Figure 11. Pressure wave intensity in front of the filter ($p_{initial} = 18$ psi).

Figure 12. Pressure wave intensity in front of the filter ($p_{initial} = 37$ psi).

Figure 13. Pressure wave intensity in front of the filter ($p_{initial} = 60$ psi).

TABLE 1
Specifications for an Isokinetic Particulate Sampling System

Maximum Inlet Gas Temperature	1,800°F
Maximum Inlet Gas Pressure	200 psig
Gas Flow Range	2,000 - 30,000 scfh
Maximum Gas Temp. @ Filter	1,000°F
Typical Sample Rate	One Sample per Hour
Gases to be Sampled	Exhaust Gases from Coal Combustion and Gasification (Reducing and Oxidizing)
Electrical Classification (NFPA)	Class I, Div. 2, Group B
Applicable Codes	ASME B31.3 Piping Code

	17			
1	16		FLOW CONTROL VALVE	
1	15		ORIFICE METER	
1	14		DRY GAS METER	
1	13		FLOW METER	
1	12		OIL TRAP WITH INDICATOR	
1	11		SAMPLING PROBE ASSEMBLY	
2	10		HEAT TRACE LINE	
1	9		HEATER, SPLIT SHELL, CERAMIC	
1	8		PARTICULATE SAMPLING ASSEMBLY	
1	7		ADSORBER, MOLECULAR SIEVE	
1	6		ADSORBER, ACTIVATED CARBON	
1	5		BUBBLER, SILICA GELL	
1	4		BUBBLER, DRY	
2	3		BUBBLER, SOLUTION	
1	2		GAS CONDITIONING TRAIN	
1	1		POSITIONING JACK, 2 STAGE PORTABLE	
QTY	ITEM	PART NO	DESCRIPTION	MATERIAL SPEC
ENERGY AND ENVIRONMENTAL RESEARCH CENTER GRAND FORKS, NORTH DAKOTA, U.S.A.				
PARTICULATE SAMPLER ASSEMBLY				
TOLERANCES UNLESS OTHERWISE SPECIFIED FRACTIONAL: $\pm 1/16$ 3 PLC. DEC.: ± 0.005 2 PLC. DEC.: ± 0.030 1 PLC. DEC.: ± 0.1 ANGULAR: $\pm 2-1/2$ DEGREES		DRAWN BY: DMB		DATE: 1-10-92
		CHECKED BY: VRK		DATE: 1-14-92
		PROJ. MGR: GLS		DATE: 1-14-92
		APPROVED BY:		DATE:
		FINAL ASSY:		NEXT ASSY:
		FUND NO: 4358		WORK REQ: W1
		REV: 1		SCALE: 1:4
		SHEET 1 OF 1		DWG NO: 1076

Figure 14. Particulate sampling system.

4.2 Pressurized Drop-Tube Furnace

Tests of kaolin as an entrained alkali getter in atmospheric and pressurized coal combustion systems were performed during this reporting period with the EERC pressurized drop-tube furnace system. Kaolin is a clay which is composed primarily of the mineral kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5[\text{OH}]_4$). In pressurized fluid-bed combustion tests using granular filter beds, clays have been shown to be good sorbents for removing alkali compounds from the gas stream (1). In laboratory studies, kaolin has been shown to be effective not only at removing sodium compounds from the gas phase, but also in irreversibly fixing the sodium (2). Other clays are also believed to absorb sodium compounds from the furnace gas when the clay is added to the coal feed to a boiler. Emathlite has been shown to be especially good at getting sodium (2).

To be an effective getter, the clay material must not deposit once the sodium is fixed. This implies that the getting material must be composed of small particles, typically less than $5\text{ }\mu\text{m}$ in diameter. Since clay particles normally have diameters smaller than this, they would appear to be ideal getting agents. However, moist clays can be highly agglomerated due to surface moisture, so it is best if the clay feed is dry before feeding to reduce agglomeration.

Kaolin was preferred for the getting test over other types of clays because it can be found in relatively pure form, containing less alkali and alkaline earth elements which may flux the material upon heating. Also, kaolinite has a layered structure composed of a sheet of silica tetrahedra bonded on one side to a sheet of aluminum hydroxide octahedra, so it has a higher aluminum-to-silicon ratio than most other clays. Because of its higher aluminum content, its possible fusion with an ash deposit will usually increase the viscosity of the deposit, thereby weakening it. Kaolin is mined in a number of places in the United States and can be supplied in rock, dried powder, or sieved dried powder forms.

Although a small body of data is available about the getters in laboratory experiments, limited data are available about the use of kaolin under carefully controlled coal combustion conditions, and none is available about its use in pressurized coal combustion conditions. Therefore, four tests were performed to test the efficacy of kaolin as a getter in both atmospheric and pressurized coal combustion conditions and to determine the mechanism of getting. The kaolin used for these tests was provided as rock by J.M Huber Corporation of Macon, Georgia. It was dried, then ground in a mortar and pestle. Only fine powder was used for the getting experiments.

The kaolin powder was mixed with pulverized coal from the Spring Creek mine, Montana, in the ratio of 1 part kaolin to 2 parts ASTM coal ash. Spring Creek coal was chosen because it has relatively high sodium and low ash contents, and because the sodium is present in the coal as an ion associated with carboxylic acid groups in the organic structure of the coal. Because of this association, the sodium is vaporized during combustion. Vaporized sodium that encounters an ash particle is typically absorbed by the particle. However, Spring Creek coal produces little ash, so much of the sodium remains in the vapor phase in the hot zone of the combustor. In cooler regions of the boiler, it may condense homogeneously to ultimately form submicron sodium sulfate particles. There is some contention as to whether sodium hydroxide

condenses, then sulfates, or sodium sulfate directly condenses. In either case, at 1800°F, a considerable portion of the sodium is likely to be in the vapor phase. This sodium is very reactive and could cause severe corrosion of ceramic hot-gas particulate pollution control devices such as candle or cross-flow filters. Therefore, Spring Creek was chosen as a "worst-case" example of a coal that may cause alkali corrosion of ceramic hot-gas cleanup devices.

Four combustion tests were performed in all. One test each of raw Spring Creek at atmospheric pressure, coal plus kaolin at atmospheric, raw coal at 100 psi, and coal plus kaolin at 100 psi. The tests were performed in the EERC pressurized drop-tube furnace system (PDTF). The following description of the system is modified from that provided in the July through December 1991 semiannual technical progress report for the Turbine Combustion Phenomena project being performed under the Cooperative Agreement at the EERC.

The pressurized drop-tube furnace (PDTF) is capable of operating under the following conditions:

Temperature: ambient to 2732°F (1500°C)
Pressure: ambient to 300 psia (20.4 atm.)
Oxygen: 0-20 mol%
Gas Flow: 0 to 7.8 scfm (220 L/min)
Residence Time: 0 to 5.0 sec

- Optical access at any residence time
- Provision for char and ash collection
- Provision for ash deposition studies

A drawing of the PDTF facility is given in Figure 15. The entire PDTF is constructed of standard 24" and 6" flanged pipe sections. The large pressure vessel contains the electrically heated furnace sections of the PDTF as shown in Figure 16. Figure 17 is a photograph of the PDTF pressure vessel. The walls of the vessel are water-cooled to dissipate the heat from the furnaces. Optical access is provided by four 3" diameter ports in the pressure vessel. The optical sight ports are located below the secondary air preheater and top two furnace sections and above one furnace to reduce the temperature gradient across the optical access section. Electrical power is supplied to the furnaces through terminals in the bottom blind flange of the pressure vessel.

Above the large pressure vessel is the fuel injector section. The injector is a one-inch-diameter water-cooled probe sheathed in high-temperature insulation. Figure 18 is a photograph showing the translating mechanism used for raising and lowering the injector into the ceramic tube inside the furnace assembly. The injector may be retracted completely out of the furnace when not in use, or may be lowered into the furnace to give a residence time between zero and 5.0 seconds. Small viewports in the pipe crosses at the bottom and top of the injector section allow visual inspection of the probe and the sample-feeding behavior.

Below the large pressure vessel is a sampling probe assembly and translation mechanism. The construction details of the probe are shown in Figure 19. The sampling probe tip is interchangeable to allow ash deposit or fly ash samples to be collected without removing the entire sample probe. For the

Figure 15. Pressurized drop-tube furnace process schematic.

Figure 16. Furnace assembly in PDTF vessel.

Figure 17. Photograph of PDTF pressure vessel.

Figure 18. Photograph of PDTF translating mechanisms.

entrained getter tests, fly ash samples were collected and size-segregated on-line with a series of two cyclones and a final nylon filter. The sampling probe may be raised to the level of the optical access ports and retracted completely from the furnace for the removal of sample deposits or when not in use. Two pipe crosses with small sight ports allow inspection of the collection probe operation, and the removal of a blind flange provides access for the removal of sample deposits.

The sample feeder assembly is a blank flanged 6" pipe cross pressurized to slightly above the furnace pressure with gas connections to the furnace assembly. Figure 19 also shows the sample feeder pressure vessel located next to the sample injector translating mechanism. Figure 20 is a schematic of the coal feeder used in the PDTF. The design allows the actual sample feeder to be constructed of lightweight material, since it does not have to withstand more than slight pressure differentials. A small sight port allows inspection of the feeder operation, and the removal of a blind flange gives access to the vessel for filling or adjustment of the feeder. The lightweight feeder can then hang from a load cell in the pressure vessel to provide a continuous record of the sample feed rates. The gas composition and flow rate of gas into the PDTF is controlled by oxygen and nitrogen mass flow controllers. Gas composition can be controlled between 0-20 mol% at flow rates up to 220 L/min. The furnace pressure is controlled by a letdown control valve at the exit of the furnace.

Figure 19. Schematic of PDFIF sampling probe with interchangeable tips.

Figure 20. Schematic of coal feeder for pressurized drop-tube furnace.

Average PDF conditions during the four alkali gettering tests are shown in Table 2. The excess air for the test of the raw Spring Creek coal at atmospheric averaged a negative 25%, indicating a fuel-rich condition for those tests. This may affect the phases that would form as compared to those that would form under oxidizing conditions, but is not expected to affect the size distribution of the sodium-rich phases, so the measured gettering effect is believed to reflect the level that would have been measured if the test were run in fuel-lean conditions. The temperatures reported for the separate furnaces are the temperatures measured at the wall of the central alumina tube. Zone 1 is at the top of the furnace, Zone 4 at the bottom where the collection probe is placed. The lower temperatures measured in Zone 3, optical section, and Zone 4 during the pressurized runs are caused by air influx through cracks in the optical system from the relatively cool space between the furnace and the pressure shell. The lower temperatures may have reduced the amount of gettering that would have occurred at pressure if there had been no air influx.

TABLE 2
Average Test Conditions for Alkali Gettering Tests
in the EERC Pressurized Drop-Tube Furnace System

	Raw Coal 2 psig	Coal+Kaol. 2 psig	Raw Coal 109 psig	Coal+Kaol. 109 psig
Feed Rate (g/min)	1.0	0.52	0.79	0.57
Excess Air (%)	-25	46	660	990
Zone 1 Tube T (°C)	1497	1497	1498	1498
Zone 2 Tube T (°C)	1497	1498	1494	1498
Zone 3 Tube T (°C)	1495	1496	1176	1212
Optical Zone T (°C)	1040	1061	921	1053
Zone 4 Tube T (°C)	1097	1097	903	981
Residence Time (s)	2.1	2.1	2.3	2.3

Figure 21 shows the percent of the total ash (corrected for unburned carbon) that was collected in each cyclone for each test. The bars represent the values for the raw coal tests, the lines represent the values for the test of the coal/kaolin blend. Because different flow rates were used for the atmospheric tests versus the pressurized tests, the cut points of the cyclones were different, so the data should not be used to determine changes in weight distributions due to pressure, only changes due to the addition of the kaolin. Attempts to measure the actual size distributions of the collected samples via laser light scattering (Malvern) were not completely successful because of particle agglomeration. In general, however, particles collected in Cyclone 2 (larger cyclone) had diameters greater than 10 microns; in Cyclone 5 (smaller cyclone) the diameters were between 1 and 10 microns; and on the filter they were less than one micron in diameter.

(a) Wt% of ash in each size fraction in the atmospheric pressure tests.

(b) Wt% of ash in each size fraction in the high-pressure tests.

Figure 21. The percent of the total ash collected in each size fraction for the tests of kaolin as an alkali getter.

In both pressure and atmospheric tests of the raw Spring Creek coal, approximately 3/4 of the ash was collected in the larger cyclone with the remainder split over the smaller cyclone and filter. At both pressures a shift toward the middle (Cyclone 5) range of ash particles occurs when kaolin is added. The size shift occurs because the kaolin predominantly ends up in this size range in the ash. The effects of the addition on ash composition are illustrated in Figure 22. The figure contains 2 three-dimensional bar graphs showing the major element compositions of each size fraction of ash for each of the four graphs. Figure 22a presents data for the atmospheric pressure tests, Figure 22b for the high-pressure tests. In each graph, the front row of data gives compositions of the raw coal samples, the back row for the coal plus kaolin tests. For each element (reported as an oxide) within each data set, the three bars represent the compositions of the larger cyclone, smaller cyclone, and filter samples respectively moving from left to right. Other elements were either present in quantities of less than 5% or did not show any gettering behavior.

Figure 22 indicates only minor changes in ash composition versus size due to pressure differences. Because different size ranges were collected in the cyclones at different pressures, the influence of pressure on these changes cannot be determined unambiguously. However, all size-related variations are maintained when pressure is changed. As is true with most U.S. low-rank coals, silica is more concentrated in the largest size range than in the smaller ranges. The increases in silica and alumina contents in the Cyclone 2 and Cyclone 5 samples indicate that most of the kaolin that was added in the gettering tests ended up in those size ranges, primarily in Cyclone 5 as indicated by the size distribution data given in Figure 21. Unlike silica and alumina, elements such as sodium and sulfur that vaporize at some point during combustion tend to concentrate in the smallest size range. XRD indicates that sodium sulfate is the major crystalline constituent of this range. Much of the sodium sulfate likely formed through cooling during sample collection, either through homogeneous nucleation of sodium hydroxide which then sulfated, or by direct nucleation of the sodium sulfate. Because cooling rates are so rapid and no residual sodium hydroxide was indicated by XRD, the latter scenario is more probable.

To determine the efficacy of the kaolin additions in gettering, the weight distribution of elements among the different size ranges must be used. Figure 23 shows two combination bar-line graphs that illustrate the weight percent of the major elements that were collected for each test in each size fraction. Like Figures 21 and 22, two graphs are used, one for the pressurized tests, the other for the atmospheric tests. The bars represent the values for the raw coal tests, the lines represent the values for the test of the coal/kaolin blend. For each element, the three data points are for the larger cyclone, the smaller cyclone, and the filter, moving from left to right.

Silicon, aluminum, and calcium all tend to be predominantly concentrated in the larger particles, with negligible fractions present in the submicron particles. In contrast, large percentages of the sodium, sulfur, and chlorine are found in the smallest particles. Sulfur was bimodally distributed, most likely present as calcium sulfate in the largest particles and as sodium sulfate in the smallest particles. Because the cyclones had different size cut points for the atmospheric versus pressurized tests, the effects of pressure on the size distributions of the elements are somewhat ambiguous. It

EERC No. JH08135-042-S

(a) Major element composition of the ash in each size fraction in the atmospheric pressure tests.

EERC No. JH08134-042-S

(b) Major element composition of the ash in each size fraction in the high-pressure tests.

Figure 22. The major element composition of the ash collected in each size fraction for the tests of kaolin as an alkali getter.

(a) Wt% of each element in each size fraction in the atmospheric pressure tests.

(b) Wt% of each element in each size fraction in the high-pressure tests.

Figure 23. The weight percent of each element collected in each size fraction for the tests of kaolin as an alkali getter.

is only clear that the weight distributions of all elements except chlorine among the different sizes are not strongly affected by pressure. In the raw coal tests, chlorine shows the only significant size shift, from larger to smaller particles at higher pressures. The chlorine-containing particles in the smallest size range probably formed during quenching of the gas during sample collection, indicating that at higher pressure more chlorine (probably as chloride) may exist in the gas phase than at atmospheric pressure. However, this conclusion is only preliminary at this point because there may have been some interference in the test data for chlorine.

The most important conclusion about the gettering tests is that sodium is shifted strongly away from the smallest particles by the addition of kaolin. If we assume that the sodium sulfate in the smallest size fraction formed when the gas was quenched during collection, then one half of the sodium was removed from the gas phase due to the kaolin addition. This result holds both at atmospheric and higher pressure. Most of the sodium was shifted to the 1- to 10-micron size range, which is where the kaolin is concentrated. The shift in sulfur from the smallest to the largest size ranges indicates that the sodium was chemically combined with the kaolin, probably in the high-temperature zone, and that the kaolin did not merely serve as a condensation surface for sodium sulfate. Because much of the sodium was removed from the gas phase, the sulfur shifted to the largest size range by sulfating additional quantities of the calcium-rich particles.

4.3 Thermochemical Equilibrium Modeling: PHOEBE Database Modifications

In the area of thermochemical equilibrium modeling, the following objectives had been set forth under Task D:

- 1a Improve PHOEBE database
- 2b Run simulations

Both items were addressed this fiscal year and are now complete. Item 1a, the improvements to the PHOEBE database, required a substantially (approximately 4 months) longer period of time than had been originally anticipated. However, the database now contains about 850 species, which is a threefold increase from its former size of about 270 species. Additionally, the database has also been thoroughly cross-checked. Validation tests have also been conducted and the database modified depending on the results of these tests. We also wish to emphasize that we expect the updating and validation process to be an ongoing activity throughout the lifetime of this (and possible other) projects.

The thermodynamic systems simulations of Item 2b have also been completed. Initially, very simple systems (like water, gas mixtures, etc.) with well-characterized thermodynamic behavior were simulated to validate the correctness of the overall PHOEBE algorithm as well as to optimize the standard free energy of formation values for many of the species in the database. A total of about 20 such simple systems were simulated. During this stage, the algorithm also underwent a few iterations of revisions and changes. Two real-life systems were selected for the final phase of this task item and their equilibrium behavior simulated. A comparison of the simulation results with the experimental phase diagrams shows quite acceptable results, the largest error in the simulated results being about 23%.

A list of chemical compounds relevant to advanced combustion systems was compiled. A variety of vapor and liquid-phase species were specifically chosen to better represent fluidized-bed combustion systems. The requisite free energy of formation (FEF) data for each species were also collated and entered into the database. The current PHOEBE database contains approximately 370 chemical compounds with an average of more than two physical phases (gas, liquid, or solid) per compound. This makes a total of roughly 800 species, which is a threefold increase over the original database. Appendix A is an index list of the database sorted by the names of the chemicals, and Appendix B is an index list of the database sorted by formulas.

The original PHOEBE database was modified to a Freeform ASCII database (FAD). This has the advantage that any conventional text-editing software can be used to edit the database. Also, since almost any text editor or word processor may be used to update, modify, or edit the database, specialized software to perform these tasks becomes redundant.

A database management utility that performs searching, retrieval, indexing, etc., was written (in C), debugged, tested, and is fully operational. Although these tasks can also be accomplished by some of the more advanced word processors, their specialized nature prohibits their execution by generic text editors.

Routines to curve-fit the free energy of formation data of the species have also been written. These routines allow a wide variety of representations (linear, polynomial, rational, logarithmic, etc.). The curve-fit representations of the FEF data can thus be chosen in the most optimal manner. In most cases, the curve-fitted FEF data are used, if need be, at the computation level.

4.3.1 Database Format Change

The advantages of FADs are twofold. First, since the database is simply an ASCII file, no specialized utilities are needed to maintain and manage the database, and the database can be transported to other operating systems or environments with no or minimal portability problems. Second, since data are entered in an arbitrary manner (with no fixed record or block size, etc.), adding, modifying, or updating entries in the database can be performed with any text editor or word processor. Once again, no specialized routines to perform these tasks are necessary. It may be noted that altering the record structure, which is quite complicated in the case of databases with fixed format records, is also trivially accomplished. Finally, since data for all of the fields of a record or chemical are often unavailable, the data entry process is also simplified to the extent that only available data need be input.

Thus each chemical in the PHOEBE database is viewed as a record, but without the limitations of fixed size and fixed number of fields. In turn, each record contains fields comprising two parts: a field identifier prefix (FIP) and the value for that field. Field identifier prefixes, as the name indicates, serve to identify the field for which the data are being entered. All FIPs start with the "dot" or "period" character (ASCII 0 H) and are followed by one or more alphabetic characters that are chosen to serve as acronyms for the field. For example, the FIP ".n" serves to identify the "name" field of the chemical, while the FIP ".f" serves to identify the

"formula" field of the chemical. Table 3 gives the list of FIPs and their explanations that are currently being used in the PHOEBE database.

TABLE 3
Field Identifier Prefixes (FIPs) and Explanations

<u>FIP</u>	<u>Explanation</u>
.n	Name of Chemical
.f	Formula of Chemical
.mp	Melting Point
.bp	Boiling Point
.p	Phase (Solid/Liquid/Gas) of Chemical
.r	Reference Citation for Data for Chemical
.v	Free Energy of Formation (FEF) Value(s) for Chemical
.end	End of Data for Chemical

As regards the value part of a field, the user simply enters the relevant data for a field subsequent to entering the FIP. For instance, for the FIP ".n" (the "name" field), the user will enter the chemical's name, while for the ".f" or "formula" field, the value part is the chemical's formula. A sample data entry for these two fields might look as follows:

```
.n Pyrite  
.f FeS2
```

Note that one or more spaces are mandatory between the FIP part and the value part of a field.

The FIP ".end" is a specialized prefix. It has no value part and is best thought of as not being an FIP at all. It is used to delineate the end of a record; that is, it is used to mark the end of data for each chemical. In principle, the use of such an "endmarker" is not necessary. However, the resulting algorithmic complexity in recognizing "end of record" without its use was sufficiently severe that it was deemed necessary.

To bring this discussion on the organization of the PHOEBE database into perspective, the actual data entry for aluminum has been extracted from the database and listed in Table 4.

4.3.2 Additions to Database

The original PHOEBE database contained approximately 130 chemicals (about 270 species) and was configured to analyze primarily the fly ash equilibrium behavior in pulverized coal- (PC) and cyclone-fired systems. However, a wide variety of condensed and vapor-phase species were not included due to lack of available data. Also, the emphasis was placed on condensed rather than vapor-phase components.

TABLE 4

PHOEBE Database: Record Entry for Aluminum

.n	Aluminum						
.f	Al						
.mp	933.25 ^a						
.bp	2793.0 ^a						
.p	s						
.r	Janaf						
.v	0.0 ^{b,c}	0.0	0.0	0.0	0.0	0.0	0.0
	0.760	1.878	2.951				
.p	ℓ						
.r	Janaf						
.v	7.180 ^{b,c}	6.053	4.926	3.798	2.671	1.535	0.384
.p	g						
.r	Janaf						
.v	288.816 ^{b,c}	275.243	261.785	248.444	235.219	222.112	209.126
	197.027	185.422	173.917	162.503	151.172	139.921	128.742

^a Melting and boiling points are in K.

^b FEF values are in kJ/mol and are in 100 K intervals starting at 300 K.

^c Not all the available FEF values are listed.

In contrast, PFBC and other advanced systems operate at elevated pressures, up to even 50 atmospheres, and it thus becomes necessary to analyze the probable phase and species distributions in these systems more critically. A simple case in point is the classic textbook example of the depression of the boiling point of water at elevated altitudes (lower atmospheric pressures) and its converse, the raising of the boiling point at higher pressures.

As a general rule, systems at elevated pressures exhibit critical behavior or phase transformations at higher temperatures as compared to systems at standard atmospheric pressure. The temperature ranges of condensed phases are thus usually prolonged, and melting is also usually skewed toward higher temperatures. Such considerations become especially important in regards to chemicals exhibiting thermal decomposition (carbonates, nitrates, hydroxides, etc.).

The selection of additional species to be included in the PHOEBE database was influenced by the higher operating pressures and the importance of alkali and reduced species in advanced systems. New species most relevant to these combustors were selected, and a literature search was conducted to collate the FEF and other data for these species. The primary sources of data references were Chase and others (3), Robie and others (4), Barin and Knacke (5), Hastie and others (6), and Kubaschewski and Alcock (7). The FEF data for an additional 240 chemicals have been now included in the database, so that the

current chemical count stands at 370 with about 800 species. This represents, approximately, a threefold increase in the size of the database.

In some cases, the FEF data over the entire range of 300 to 3000 K were unavailable. A variety of approximation and extrapolation techniques were adopted to ensure that data were available over the entire temperature range. It must be noted that the temperature range of 300 to 3000 K represents metastable regimes for almost all species (excluding perhaps some vapor-phase ones), and, hence, the requisite FEF data must usually be approximated.

The extrapolation technique used in many cases was that of graphical extrapolation wherein the formational free energy values are curve-fit to canonical or standard curves and the resulting curve extrapolated over the entire temperature range. In cases where the data were almost complete or almost linear, linear extrapolation was used to extend the range of the values. In the case of some vapor-phase species, however, since literature data were totally unavailable, the free energy values were computed from first principles as outlined in Mayer and Mayer (8) and McBride and Gordon (9).

In the case of a few liquids, data below the melting point were approximated by using a glass transition temperature ($\sim 7/10$ the melting point) and determining the free energy values by integrating the isobaric specific heat (C_p) data of the solid. It may be noted that the liquid may not necessarily cool to a glassy state in the metastable regime; nevertheless, as admonished by Chase and others (3), the use of a glass transition temperature is necessary to prevent an entropy paradox wherein the free energy of the thermodynamically more stable solid phase is higher than its metastable counterpart.

4.3.3 Database Utilities

A database search and sort utility and another utility to curve-fit the species FEF data have been implemented and are fully operational. As remarked earlier, these utilities are specific to the database and can be used to conduct a wide range of searches as well as select optimal curve fits for the FEF data.

The curve-fitting routines attempt to approximate the free energy data as a smooth function of temperature by regression. The basic ideas are as follows. Let μ° be the true FEF function and $f_1, f_2, \dots, f_p$ a set of P -functions ("basis" functions). The approximate $\tilde{\mu}$ to the n FEF values is then defined by

$$\tilde{\mu} = \sum_{\alpha=1}^P c_{\alpha} f_{\alpha} \quad [\text{Eq. 1}]$$

where the coefficients $c_1, \dots, c_p$ are determined by the condition that the residual R is defined by

$$R = |\mu^o - \mu| = |\mu^o - \sum_{\alpha} c_{\alpha} f_{\alpha}| \quad [\text{Eq. 2}]$$

be a minimum, where $\|x\|$ denotes the norm of x .

Conventionally, the norm in Eq. 2 is taken to be the ℓ_2 or Euclidean norm, which then leads to a multilinear regression problem. With other norms, such as the ℓ_1 or ℓ_{∞} norms, the problem becomes nonlinear, and nonlinear minimization algorithms (such as the Marquardt-Levenberg algorithm) need to be utilized. Since the PHOEBE curve-fit routines are general purpose routines, both the linear and nonlinear cases are handled without any difficulty.

As to the choice of the approximating functions $f_1, \dots, f_p$, it may be mentioned that three particular sets of approximants are prevalent in the literature. The first is the linear approximant

$$f_1 = 1, f_2 = T,$$

the second is the log-linear approximant

$$\begin{aligned} f_1 &= 1 \\ f_2 &= T \\ f_3 &= T \ln T \end{aligned}$$

and, finally, the third is the log-hyperbolic-cubic approximant

$$\begin{aligned} f_1 &= 1/T \\ f_2 &= 1 \\ f_3 &= T \\ f_4 &= T^2 \\ f_5 &= T^3 \\ f_6 &= T \ln T \end{aligned}$$

Of these three, the 6-term log-hyperbolic-cubic approximant appears to be emerging as the accepted standard.

The PHOEBE database search and sort routines have also been implemented as fairly general purpose utilities. These allow the user to search the database in a variety of ways including searching by chemical name, by formula, by melting and boiling points, and by phase. The Boolean operations AND, OR, and NOT can also be used in specifying search criteria so that chemicals and species can be located very efficiently. In addition, a rudimentary regular expression matching facility is also included, enabling the user to specify search criteria in terms of regular expressions as well.

Currently, three sort options are available to the user to sort the chemicals in the data. One of these, of course, is to sort by the names of the chemicals, the other is to sort by the formulas of the chemicals, and the third option is to sort by the number of elements comprising the chemicals. Additional sorting categories, such as sorting by molecular or formula weight, or sorting by melting point, etc., can be included, although, in contrast to the search utility, no provision has been made to permit a dynamic sort

specification facility. The index lists in Appendices A and B have been constructed using the PHOEBE database sort utility.

4.4 PHOEBE Algorithm Extensions

The modules to enable equilibrium computations to be performed under different system pressures have been completed and incorporated into PHOEBE. These modules are, technically, "supervisory" modules in that the equilibrium behavior of the system under different system pressures is computed based upon user-specified or user-selectable models for the equation of state of the system. Thus a wide variety of equations of state, empirical and theoretical, can be simulated and tested, allowing for the possibility of optimal equations of state. The debugging and testing of these modules have been completed.

The entire set of PHOEBE routines, originally written in FORTRAN, have been rewritten in C to extend the portability of the package as well as to take advantage of the emerging object-oriented languages (such as C++). The overall algorithm has also been debugged and tested, and Section 4.4 describes some of the results obtained.

A preprocessor module has also been added to PHOEBE that allows the user to specify and work with thermodynamic systems in a fairly abstract manner. A given system once defined will be usable as a system in and of itself, or as part of a larger system. Some of the more common systems, such as "air," "xrf," "ultimate," etc., have been predefined and may be used as such. Thus, starting with simple systems, a whole hierarchy of systems can be defined leading to more complex systems such as coal blends, systems with additives, and so on.

Three major modifications have been carried out at the algorithmic level. The entire set of PHOEBE routines has been rewritten in C, modules to handle variations in system pressure have been incorporated, and an input data preprocessor has been added that permits abstract system definition and usage. Sections 4.3.2 and 4.3.3 describe, respectively, these modifications.

4.4.1 Original Algorithm Description

The original PHOEBE routines had been coded in FORTRAN. A menu-driven I/O preprocessor, written in ASSEMBLER, served as the user interface to the PHOEBE kernel. Maintenance, updating, and portability issues had been raised even then, but, for lack of other alternatives, were set aside. With the current proliferation of and advancement in windowed operating systems, Graphical User Interfaces (GUIs), and object-oriented languages, portability issues have become important. Thus one of the objectives of this task was the "modernization" of PHOEBE in terms of rewriting it in a more flexible and modern language.

The choice of C as the programming language was based on two reasons. One, the standardization of C is well in place, and a large number of operating system environments support the language so that the portability requirement is easily met. Two, interfacing with object-oriented languages, especially C++, is trivially accomplished, so that constructing friendly interfaces is also relatively simple. As mentioned earlier, the PHOEBE routines have been rewritten in C and a majority of them tested and debugged

during the coding stage itself. The overall program also has been tested for algorithmic correctness.

The central computational module in PHOEBE is an optimization routine that minimizes the Gibbs Free Energy of the system of interest. This minimization is achieved by varying the amounts of the species in the various phases until the smallest possible value of the free energy is achieved. More precisely, if the system comprises k phases whose free energies are G^1 , G^2 , ..., G^k , the free energy G of the entire system is approximated as:

$$G = \sum_{\alpha=1}^K G^{\alpha} \quad [\text{Eq. 3}]$$

Note that Eq. 3 is exact if there are no phase-phase interactions or if these interactions are negligible.

The individual phase free energies G^{α} are in turn given by

$$G^{\alpha} = \sum_{i=1}^{N^{\alpha}} (\mu_{oi}^{\alpha} + \ln a_i^{\alpha}) n_i^{\alpha} \quad [\text{Eq. 4}]$$

$a_i^{\alpha} =$

where N^{α} is the number of species in the phase, n_i^{α} is the (molar) amount of species i in the phase, μ_i^{α} is the (standard) FEF of species i , and a_i^{α} is the activity of i within phase α . The ideal approximation to G^{α} arises when the activities a_i^{α} are approximated by:

$$a_i^{\alpha} = \begin{cases} 1, & \text{when } \alpha \text{ is a pure condensed phase} \\ \frac{n_i^{\alpha}}{\sum_j n_j^{\alpha}}, & \text{when } \alpha \text{ is a solution phase} \\ \frac{P}{P_o} \left(\frac{N_i^{\alpha}}{\sum_j n_j^{\alpha}} \right), & \text{when } \alpha \text{ is a gas phase} \end{cases} \quad [\text{Eq. 5}]$$

where P and P_o are, respectively, the system pressure and the standard pressure.

The species amount or abundance vector n_i^{α} is not completely arbitrary, but has to satisfy the so-called mass balance and nonnegativity constraints. The mass balance constraints are linear equalities connecting the elemental amounts $b_1, b_2, \dots, b_M$ (where M is the number of elements in the system) and the n_i^{α} . These can be succinctly expressed as:

$$b_a = \sum_{\alpha=1}^{\kappa} \sum_{j=1}^{N^{\alpha}} S_{a,j}^{\alpha} n_j^{\alpha} \quad [\text{Eq. 6}]$$

where $S_{a,j}^{\alpha}$ is the stoichiometry coefficient of element a in species j in phase α . The nonnegativity constraints

$$n_j^{\alpha} \geq 0, \alpha = 1, \dots, \kappa, j = 1, \dots, N^{\alpha} \quad [\text{Eq. 7}]$$

are conventionally not regarded as explicit constraints, but treated implicitly in the minimization algorithm. A more detailed account of this and other related aspects can be found in Ramanathan and others (10,11) and the references contained therein.

4.4.2 Pressure Calculations

It may be recalled from classical thermodynamics that the Gibbs Free Energy G of a thermodynamic system is defined as:

$$G = H - TS$$

where H is the enthalpy, T the temperature, and S the entropy of the system. In general, G is a function of the temperature T , the pressure P , and the molar amounts n_i^{α} of the species. Since almost all of the data on the free energy of formation of substances are for a particular pressure (usually, the standard atmospheric pressure), extrapolation of this data is necessary in order to study the equilibrium behavior of systems at elevated pressures.

This extrapolation is based on the fact that the pressure derivative $\frac{\partial G}{\partial P}$ of the free energy is the volume V of the system:

$$\frac{\partial G}{\partial P} = V \quad [\text{Eq. 8}]$$

so that,

$$G(T, P) = \int_{P_0}^P V dP + G(T, P_0) \quad [\text{Eq. 9}]$$

Eq. 9 is the key expression that permits the computation of the free energy for different pressures P , once the value $G(T, P_0)$ is known at a particular pressure P_0 . In order to perform the integration in Eq. 9, an explicit expression of the volume in terms of pressure is needed. This is usually obtained from an equation of state, either empirical or theoretical, for the system.

A variety of state equations are available in the literature, starting with the Van der Waals equations of state for (real) gases, to the Murnaghan

model (12) for condensed phases. The Murnaghan model, in particular, is predicated on the assumption that the bulk modulus B is an affine function of the pressure; i.e.,

$$B(T,P) = B_0(T,P_0) + nP$$

where $B_0(T, P_0)$ is the bulk modulus at the standard pressure P_0 and n is the pressure coefficient (usually about 4). Since the bulk modulus is related to the pressure derivative of the volume through

$$\frac{1}{V} \frac{\partial V}{\partial P} = \frac{1}{B} = \frac{1}{B_0 + nP}$$

integration of the above equation yields

$$V(T,P) = V_0(T) \left(1 + \frac{nP}{B_0}\right)^{-\frac{1}{n}} \quad [\text{Eq. 10}]$$

which may then be used in performing the integration in Eq. 9.

As remarked earlier, the pressure module routines in PHOEBE are primarily supervisory and can accommodate any user-specified equation of state. Such a capability is almost a must if formational free energies are to be computed at different pressures for a plethora of chemical compounds ranging over the spectrum of solid, liquid, and gaseous phases. Although some of the more standard equations of state are already built into the system, it is expected that an expanded library of such state equations will become a standard feature in PHOEBE in the near future.

4.4.3 Preprocessor Utilities

A significant enhancement in the area of problem statement and formulation in PHOEBE is the addition of preprocessor utilities that allow abstract (thermodynamic) system definitions and usage. Complex systems can thus be analyzed quite easily and naturally, and, since the facility is a dynamic one, a library or database of systems can be predefined and used in a straightforward manner.

Conventionally, one of the primary inputs to PHOEBE, the abundance or amount vector, had been specified at the elemental level, or in some cases at the oxide level. Algorithmically, this is the form of input that is needed and accepted by PHOEBE. However, from an application standpoint, this input format is quite inconvenient and cumbersome in many cases. For instance, in order to analyze the effect of additives such as alkali getters on performance, the most natural statement of the problem will be to define a thermodynamic system whose "components" are the coal and the envisaged additive. Another example is the analysis of coal blends. In this case, the "components" are the coals to be blended. There are many instances where an extended definition of a "component" of a thermodynamic system simplifies and, in some cases, even clarifies the problem formulation.

To accommodate these cases, preprocessor utilities have been added to PHOEBE that ease the drudgery of data entry and enable the user to specify the problem in a very natural manner. These utilities work by constructing a hierarchical diagram or a system definition tree (SDT) that contains the information relating a system to its subsystems and ultimately down to the basic components: the elements. (In the terminology of tree-processing, the elements constitute the "leaves" or "external nodes" of the SDT). Note that the recursive definition of trees implies that SDTs can be imbedded to any arbitrary level, limited only, perhaps, by available memory. A typical SDT starts with the highest-level abstract specification and successively gets more and more concrete until finally the definitions reduce to lists of chemical formulas or elements. For instance, the following definition-set:

```

Fuel      = Air, Coal
Coal      = Ultimate, Ash
Ultimate  = H2O, CO2, SO2, NO2
Ash       = Al2O3, SiO2, MgO, CaO
Air       = N2, O2, CO2

```

is an example of an abstract thermodynamic system, "fuel," and illustrates the utility, flexibility, and power of abstract system definitions. The SDT of this system has as its root the node "fuel" with two principal branches, connecting the (sub) systems "air" and "coal." Figure 24 displays the SDT of this model system. In the figure, the elemental nodes or leaves of this tree are also displayed.

Figure 24. An example system definition tree (SDT).

In some cases it proves useful to define systems with a fixed stoichiometry between its subsystems. For example, the thermodynamic system "air" is commonly considered to be a system containing O_2 , N_2 , H_2O , and CO_2 in fixed proportions. To accommodate such fixed stoichiometry systems, a PHOEBE system definition tree is permitted to have an optional stoichiometry specification as well. Thus, for example, one can define the system "air" as:

so that the stoichiometry values (78, 21, etc.) become built into the definition of the "air" system.

4.4.4 Tests of the Database Algorithms

Two phase diagram calculations were performed with PHOEBE as part of overall program verification as well as to gain an understanding of the program's accuracy. In general, phase diagram calculations are very time intensive since the free energy of the system needs to be repeatedly minimized as the program steps through the extensive variables (like temperature and component amounts). The two phase diagram calculations that were done, for instance, took a total of 4 hours to compute (and plot). The results of these calculations are displayed in Figures 25 and 26.

Figure 25 is a plot of the experimental versus PHOEBE-predicted phase diagram for the binary system $Al_2O_3 - SiO_2$. (The solid lines are the experimentally determined phase boundaries while the dotted lines are the predicted phase boundaries.) Figure 26 is a plot of the experimental versus predicted phase diagram of the system Na_2SiO_4 . (This represents a cross-section of the ternary system $Na_2O - Al_2O_3 - SiO_2$.) As can be seen from these figures, the predicted values track the experimental values fairly well with the largest error being about 23%. It should also be noted that both these systems were assumed to behave ideally (i.e., with unit-activity coefficients) so, necessarily, we expect errors in the predicted values since it is well known that these systems are nonideal. Additionally, it must also be borne in mind that inherent inaccuracies exist in the FEF values in the database. All in all, therefore, it can be concluded that PHOEBE provides acceptably accurate representations of the equilibrium behavior of multiphase, multicomponent systems.

5.0 FUTURE WORK

5.1 Particulate Control

Future work will consist of making modifications to the test loop to improve outlet particulate loading data, relocating some of the instrumentation, adding additional instrumentation, building the particulate sampling system, continued testing of filter elements, performance characterization of the heated backpulse system, and studying various alkali issues as they relate to advanced cycle power systems.

The design work required to relocate the test loop cannot be done until the location of the test loop is determined. This is contingent upon the size, shape, and location of the TRTU. For this reason, some of the design

$\text{Al}_2\text{O}_3\text{-SiO}_2$

Figure 25. A plot of the experimental PHOEBE-predicted phase diagram for $\text{Al}_2\text{O}_3\text{-SiO}_2$.

$\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$

Figure 26. A plot of the experimental vs. predicted phase diagram for Na_2SiO_4 .

work remains unfinished. As soon as the necessary TRTU parameters are identified, the design work on the test loop will be completed. The test loop is expected to be in place and operational in time to be used in conjunction with the initial testing of the TRTU.

High-temperature flange connections for the filter modules are also being designed in order to operate at the extreme conditions of the test loop and to comply with B31.3 piping codes. This will consist of finite element modeling of flange connections to determine thermal stresses and creep phenomena.

5.2 Alkali Gettering

The short-term objective is to construct a coal-water slurry feed system for the PDTF to permit long-duration tests of alkali corrosion of ceramic materials in atmospheric and pressurized coal combustion systems.

5.3 Thermochemical Modeling

No specific task or action item is proposed. Instead, it is expected that PHOEBE will be extensively used as a general tool for the thermodynamic analyses of advanced combustion systems and, specifically, as an optimizer for the selection of alkali gettering materials.

6.0 REFERENCES

1. Lee, S.H.D; Johnson, I. "Removal of Gaseous Alkali Metal Compounds from Hot Flue Gas by Particulate Sorbents," *Journal of Engineering for Power* 1980, 102, 397-402.
2. Punjak, W.A.; Shadman, F. "Aluminosilicate Sorbents for Control of Alkali Vapors During Coal Combustion and Gasification," *Energy and Fuels* 1988, 2 (5), 702-708.
3. Chase, M.W., Jr.; Davies, C.A.; Downey, J.R., Jr.; Frurip, D.J.; McDonald, R.A.; Syverud, A.N. *JANAF Thermochemical Tables*, 3rd ed.; American Chemical Society, NY, 1985.
4. Robie, R.A.; Hemingway, B.S.; Fisher, J.R. "Thermodynamic Properties of Minerals and Related Substances at 285.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures," 1978, *U.S. Geol. Surv. Bull.* 1452.
5. Barin, I.; Knacke, O. *Thermochemical Properties of Inorganic Substances*; Springer-Verlag, NY, 1973.
6. Hastie, J.W.; Ondik, H.M.; Bonnell, D.W. "Development of a Ceramic Phase Diagram and Thermodynamic Data Bank," International Conference on the User Applications of Alloy Phase Diagrams, Oct. 4-9, 1988, Lake Buena Vista, FL.
7. Kubaschewski, O.; Alcock, C.B. *Metallurgical Thermochemistry*, 5th ed.; Pergamon Press, NY, 1979.
8. Mayer, J.E.; Mayer, M.G. *Statistical Mechanics*; Wiley, NY, 1957.

9. McBride, B.J.; Gordon, S. "FORTRAN IV Program for Calculation of Thermodynamic Data," NASA TN D-4097, 1967.
10. Ramanathan, M.; Kalmanovitch, D.P.; Ness, S.R. "New Techniques for Thermochemical Equilibria Predictions in Coal Ash Systems - I," *High Temp. Science, An Int'l. Journal* 1989, 28.
11. Ramanathan, M.; Kalmanovitch, D.P. "New Techniques for Thermochemical Equilibria Predictions in Coal Ash Systems II," Conference on High-Temperature Materials Chemistry, ACS Div. Fuel Chemistry, Dallas, TX, 1989.
12. Murnaghan, F.D. *Proc. Natl. Acad. Sci. USA* 1944, 30, 244.

APPENDIX A

FEF DATABASE

Chemical
Name Index

No.	Name	Formula
0	2-BUTYNEDINITRILE	C_4N_2 (g)
1	ACETYLENE	C_2H_2 (g)
2	AKERMANITE	$Ca_2MgSi_2O_7$ (s)
3	ALBITE	$NaAlSi_3O_8$ (s,l)
4	ALUMINUM	Al (s,l,g)
5	ALUMINUM CARBIDE	AlC (g)
6	ALUMINUM DICHLORIDE	$AlCl_2$ (g)
7	ALUMINUM DIOXIDE	AlO_2 (g)
8	ALUMINUM HEXACHLORIDE	Al_2Cl_6 (g)
9	ALUMINUM HYDRIDE	AlH (g)
10	ALUMINUM HYDROXIDE	$AlOH$ (g)
11	ALUMINUM MONOCHLORIDE	$AlCl$ (g)
12	ALUMINUM MONOXIDE	AlO (g)
13	ALUMINUM NITRIDE	AlN (s,g)
14	ALUMINUM OXYCHLORIDE	$AlOCl$ (s,g)
15	ALUMINUM SULFATE	$Al_2S_3O_{12}$ (s)
16	ALUMINUM SULFIDE	AlS (g)
17	ALUMINUM SULFIDE	Al_2S_3 (s)
18	ALUMINUM TRICARBIDE	Al_4C_3 (s)
19	ALUMINUM TRICHLORIDE	$AlCl_3$ (s,l,g)
20	AMIDOGEN	NH_2 (g)
21	AMMONIA	NH_3 (g)
22	AMMONIUM CHLORIDE	NH_4Cl (s)
23	AMMONIUM NITRATE	$N_2H_4O_3$ (s)
24	AMMONIUM PERCHLORATE	NH_4ClO_4 (s)
25	ANDALUSITE	Al_2SiO_5 (s)
26	ANHYDRITE	$CaSO_4$ (s)
27	ANORTHITE	$CaAl_2Si_2O_8$ (s,l)
28	ARGON	Ar (g)
29	AZIDE	N_3 (g)
30	BARITE	$BaSO_4$ (s)
31	BARIUM	Ba (s,l,g)
32	BARIUM CHLORIDE	$BaCl$ (g)
33	BARIUM DICHLORIDE	$BaCl_2$ (s,l,g)
34	BARIUM DIHYDROXIDE	BaO_2H_2 (s,l,g)
35	BARIUM MONOHYDROXIDE	$BaOH$ (g)
36	BARIUM OXIDE	BaO (s,l,g)
37	BARIUM SULFIDE	BaS (s,g)
38	BERLINITE	$AlPO_4$ (s)
39	BOEHMITE	AlO_2H (g)
40	CA-AL PYROXENE	$CaAl_2SiO_6$ (s)
41	CALCITE	$CaCO_3$ (s)
42	CALCIUM	Ca (s,l,g)
43	CALCIUM FERRITE	$CaFe_2O_4$ (s)
44	CALCIUM MONOCHLORIDE	$CaCl$ (g)

FEF DATABASE

Chemical
Name Index

No.	Name	Formula
45	CALCIUM MONOHYDROXIDE	CaOH (g)
46	CALCIUM NITRATE	CaN ₂ O ₆ (s)
47	CALCIUM OXIDE	CaO (s,l,g)
48	CARBON	C ₂ (g)
49	CARBON	C ₃ (g)
50	CARBON	C ₄ (g)
51	CARBON	C ₅ (g)
52	CARBON	C (s,g)
53	CARBON DIOXIDE	CO ₂ (g)
54	CARBON DISULFIDE	CS ₂ (g)
55	CARBON MONOXIDE	CO (g)
56	CARBON OXIDE SULFIDE	COS (g)
57	CARBON PHOSPHIDE	CP (g)
58	CARBON SUBOXIDE	C ₃ O ₂ (g)
59	CARBON SULFIDE	CS (g)
60	CARBON TETRACHLORIDE	CCl ₄ (g)
61	CARBONIC DICHLORIDE	COCl ₂ (g)
62	CARBONYL CHLORIDE	COCl (g)
63	CHALCOCITE	Cu ₂ S (s)
64	CHLORINE	Cl (g)
65	CHLORINE	Cl ₂ (g)
66	CHLORINE DIOXIDE	ClO ₂ (g)
67	CHLORINE MONOXIDE	ClO (g)
68	CHLOROETHYNE	C ₂ HCl (g)
69	CHLOROMETHANE	CH ₃ Cl (g)
70	CHLOROMETHYLENE	CHCl (g)
71	CHLOROMETHYLIDYNE	CCl (g)
72	CHLOROSILANE	SiH ₃ Cl (g)
73	COHENITE	Fe ₃ C (s)
74	COPPER	Cu (s,l,g)
75	COPPER	Cu ₂ (g)
76	COPPER CYANIDE	CuCN (s)
77	COPPER DICHLORIDE	CuCl ₂ (s)
78	COPPER HYDROXIDE	CuH ₂ O ₂ (s)
79	COPPER MONOCHLORIDE	CuCl (s,l,g)
80	COPPER OXIDE	CuO (s,g)
81	COPPER SULFATE	CuSO ₄ (s)
82	CORDIERITE	Mg ₂ Al ₄ Si ₅ O ₁₈ (s)
83	CORUNDUM	Al ₂ O ₃ (s,l)
84	CUPROUS OXIDE	Cu ₂ O (s,l)
85	CYANOGEN	CN (g)
86	CYANOGEN CHLORIDE	CNCl (g)
87	DIALUMINUM DIOXIDE	Al ₂ O ₂ (g)
88	DIALUMINUM MONOXIDE	Al ₂ O (g)
89	DIAZENE (CIS)	N ₂ H ₂ (g)

FEF DATABASE

Chemical
Name Index

No.	Name	Formula
90	DICALCIUM FERRITE	$\text{Ca}_2\text{Fe}_2\text{O}_5$ (s)
91	DICHLORINE MONOXIDE	Cl_2O (g)
92	DICHLOROETHYNE	C_2Cl_2 (g)
93	DICHLOROMETHANE	CH_2Cl_2 (g)
94	DICHLOROMETHYLENE	CCl_2 (g)
95	DICHLOROSILANE	SiH_2Cl_2 (g)
96	DICOPPER SULFATE	Cu_2SO_5 (s)
97	DIHYDROGEN PHOSPHIDE	H_2P (g)
98	DIIRON HEXACHLORIDE	Fe_2Cl_6 (g)
99	DIIRON TETRACHLORIDE	Fe_2Cl_4 (g)
100	DILITHIUM DICHLORIDE	Li_2Cl_2 (g)
101	DILITHIUM DIHYDROXIDE	$\text{Li}_2\text{H}_2\text{O}_2$ (g)
102	DIMAGNESIUM TETRACHLORIDE	Mg_2Cl_4 (g)
103	DINITROGEN OXIDE	N_2O (g)
104	DINITROGEN PENTAOXIDE	N_2O_5 (g)
105	DINITROGEN TETRAOXIDE	N_2O_4 (s,l,g)
106	DINITROGEN TRIOXIDE	N_2O_3 (g)
107	DIOPSIDE	$\text{CaMgSi}_2\text{O}_6$ (s,l)
108	DIPOTASSIUM CYANIDE	$\text{K}_2\text{C}_2\text{N}_2$ (g)
109	DIPOTASSIUM DICHLORIDE	K_2Cl_2 (g)
110	DIPOTASSIUM DIHYDROXIDE	$\text{K}_2\text{H}_2\text{O}_2$ (g)
111	DISILICON NITRIDE	Si_2N (g)
112	DISODIUM CYANIDE	$\text{Na}_2\text{C}_2\text{N}_2$ (g)
113	DISODIUM DICHLORIDE	Na_2Cl_2 (g)
114	DISODIUM DIHYDROXIDE	$\text{Na}_2\text{H}_2\text{O}_2$ (g)
115	DISULFUR DICHLORIDE	S_2Cl_2 (l,g)
116	DISULFUR MONOCHLORIDE	S_2Cl (g)
117	DISULFUR MONOXIDE	S_2O (g)
118	DOLOMITE	CaMgC_2O_6 (s)
119	ETHANEDINITRILE	C_2N_2 (g)
120	ETHYLENE	C_2H_4 (g)
121	ETHYNYL	C_2H (g)
122	FAYALITE	Fe_2SiO_4 (s)
123	FERRIC SULFATE	$\text{Fe}_2\text{S}_3\text{O}_{12}$ (s)
124	FORMALDEHYDE	CH_2O (g)
125	FORMYL	HCO (g)
126	FORSTERITE	Mg_2SiO_4 (s,l)
127	GEHLENITE	$\text{Ca}_2\text{Al}_2\text{SiO}_7$ (s,l)
128	GROSSULAR	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (s)
129	HEMATITE	Fe_2O_3 (s)
130	HEXACHLOROETHANE	C_2Cl_6 (g)
131	HIGH SANIDINE	KAlSi_3O_8 (s,l)
132	HYDRAZINE	N_2H_4 (l,g)
133	HYDROGEN	H (g)
134	HYDROGEN	H_2 (g)

FEF DATABASE

Chemical
Name Index

No.	Name	Formula
135	HYDROGEN CHLORIDE	HCl (g)
136	HYDROGEN CYANIDE	HCN (g)
137	HYDROGEN ISOCYANATE	HCNO (g)
138	HYDROGEN PEROXIDE	H ₂ O ₂ (g)
139	HYDROGEN PHOSPHIDE	HP (g)
140	HYDROGEN SULFIDE	H ₂ S (g)
141	HYDROPEROXO	HO ₂ (g)
142	HYDROPHILITE	CaCl ₂ (s,l,g)
143	HYDROXYAPATITE	Ca ₅ P ₃ HO ₁₃ (s)
144	HYPOCHLOROUS ACID	HOCl (g)
145	ILMENITE	FeTiO ₃ (s)
146	IMIDOGEN	NH (g)
147	IRON	Fe (s,l,g)
148	IRON CARBONYL	FeC ₅ O ₅ (l,g)
149	IRON DICHLORIDE	FeCl ₂ (s,l,g)
150	IRON HYDROXIDE	FeH ₂ O ₂ (s,g)
151	IRON MONOCHLORIDE	FeCl (g)
152	IRON OXIDE	FeO (s,l,g)
153	IRON SULFATE	FeSO ₄ (s)
154	IRON TRICHLORIDE	FeCl ₃ (s,l,g)
155	IRON TRIHYDROXIDE	FeH ₃ O ₃ (s)
156	JADEITE	NaAlSi ₂ O ₆ (s,l)
157	KALIOPHILLITE	KAlSiO ₄ (s)
158	LARNITE (CA-OLIVINE)	Ca ₂ SiO ₄ (s)
159	LEUCITE	KAlSi ₂ O ₆ (s)
160	LITHIUM	Li (s,l,g)
161	LITHIUM	Li ₂ (g)
162	LITHIUM ALUMINATE	LiAlO ₂ (s,l)
163	LITHIUM CARBIDE	Li ₂ C ₂ (s)
164	LITHIUM CARBONATE	Li ₂ CO ₃ (s,l)
165	LITHIUM DISILICATE	Li ₂ Si ₂ O ₅ (s,l)
166	LITHIUM HYDRIDE	LiH (s,l,g)
167	LITHIUM HYDROXIDE	LiOH (s,l,g)
168	LITHIUM HYPOCHLORITE	LiOCl (g)
169	LITHIUM MONOCHLORIDE	LiCl (s,l,g)
170	LITHIUM MONOXIDE	LiO (g)
171	LITHIUM NITRIDE	LiN (g)
172	LITHIUM OXIDE	Li ₂ O (s,l,g)
173	LITHIUM OXYNITRIDE	LiON (g)
174	LITHIUM PERCHLORATE	LiClO ₄ (s,l)
175	LITHIUM PEROXIDE	Li ₂ O ₂ (s,g)
176	LITHIUM SILICATE	Li ₂ SiO ₃ (s,l)
177	LITHIUM SODIUM OXIDE	LiNaO (g)
178	LITHIUM SULFATE	Li ₂ SO ₄ (s,l,g)
179	LITHIUM TETRAHYDROALUMINATE	LiAlH ₄ (s)

FEF DATABASE

Chemical
Name Index

No.	Name	Formula
180	LITHIUM TITANATE	Li_2TiO_3 (s,l)
181	MAGNESIOFERRITE	MgFe_2O_4 (s)
182	MAGNESITE	MgCO_3 (s)
183	MAGNESIUM	Mg (s,l,g)
184	MAGNESIUM	Mg_2 (g)
185	MAGNESIUM CARBIDE	Mg_2C_3 (s)
186	MAGNESIUM CARBIDE	MgC_2 (s)
187	MAGNESIUM DICHLORIDE	MgCl_2 (s,l,g)
188	MAGNESIUM DIHYDRIDE	MgH_2 (s)
189	MAGNESIUM DIHYDROXIDE	MgH_2O_2 (s,g)
190	MAGNESIUM DINITRIDE	Mg_3N_2 (s)
191	MAGNESIUM DITITANATE	MgTi_2O_6 (s,l)
192	MAGNESIUM HYDRIDE	MgH (g)
193	MAGNESIUM HYDROXIDE	MgOH (g)
194	MAGNESIUM MONOCHLORIDE	MgCl (g)
195	MAGNESIUM NITRATE	MgN_2O_4 (s)
196	MAGNESIUM NITRIDE	MgN (g)
197	MAGNESIUM ORTHOTITANATE	Mg_2TiO_4 (s,l)
198	MAGNESIUM OXIDE	MgO (s,l,g)
199	MAGNESIUM PHOSPHATE	$\text{Mg}_3\text{P}_2\text{O}_8$ (s,l)
200	MAGNESIUM SILICATE	MgSiO_3 (s,l)
201	MAGNESIUM SILICIDE	Mg_2Si (s,l)
202	MAGNESIUM SULFATE	MgSO_4 (s,l)
203	MAGNESIUM SULFIDE	MgS (s,g)
204	MAGNESIUM TITANATE	MgTiO_3 (s,l)
205	MAGNETITE	Fe_3O_4 (s)
206	MASCAGNITE	$\text{N}_2\text{H}_6\text{SO}_4$ (s)
207	MERCAPTO	HS (g)
208	MERWINITE	$\text{Ca}_3\text{MgSi}_2\text{O}_8$ (s)
209	METHANE	CH_4 (g)
210	METHINOPHOSPHIDE	CHP (g)
211	METHYL	CH_3 (g)
212	METHYLENE	CH_2 (g)
213	METHYLIDYNE	CH (g)
214	MULLITE	$\text{Al}_6\text{Si}_2\text{O}_{13}$ (s,l)
215	MUSCOVITE	$\text{KAl}_3\text{Si}_3\text{H}_2\text{O}_{12}$ (s)
216	NEPHELINE	NaAlSiO_4 (s,l)
217	NITER	KNO_3 (s)
218	NITRIC ACID	HNO_3 (g)
219	NITROBARITE	BaN_2O_4 (s)
220	NITROGEN	N (g)
221	NITROGEN	N_2 (g)
222	NITROGEN DIOXIDE	NO_2 (g)
223	NITROGEN MONOXIDE	NO (g)
224	NITROGEN TRIOXIDE	NO_3 (g)

No.	Name	Formula
225	NITROSYL CHLORIDE	NOCl (g)
226	NITROUS ACID	$\text{HNO}_2 \text{ (g)}$
227	NITROXYL	HNO (g)
228	NITRYL CHLORIDE	$\text{NO}_2\text{Cl (g)}$
229	OLDHAMITE	CaS (s,g)
230	OXIRANE	$\text{C}_2\text{H}_4\text{O (g)}$
231	OXYGEN	O (g)
232	OXYGEN	$\text{O}_2 \text{ (g)}$
233	OZONE	$\text{O}_3 \text{ (g)}$
234	PEROVSKITE	$\text{CaTiO}_3 \text{ (s)}$
235	PHOSPHORIC ACID	$\text{H}_3\text{PO}_4 \text{ (s,l)}$
236	PHOSPHOROUS MONOCHLORIDE	PCl (g)
237	PHOSPHORUS	P (s,l,g)
238	PHOSPHORUS	$\text{P}_2 \text{ (g)}$
239	PHOSPHORUS	$\text{P}_4 \text{ (g)}$
240	PHOSPHORUS DIOXIDE	$\text{PO}_2 \text{ (g)}$
241	PHOSPHORUS MONOXIDE	PO (g)
242	PHOSPHORUS NITRIDE	PN (g)
243	PHOSPHORUS PENTACHLORIDE	$\text{PCl}_5 \text{ (g)}$
244	PHOSPHORUS PENTAOXIDE DIMER	$\text{P}_4\text{O}_{10} \text{ (s,g)}$
245	PHOSPHORUS SULFIDE	PS (g)
246	PHOSPHORUS TRICHLORIDE	$\text{PCl}_3 \text{ (g)}$
247	PHOSPHORUS TRIOXIDE DIMER	$\text{P}_4\text{O}_6 \text{ (g)}$
248	PHOSPHORUS TRISULFIDE	$\text{P}_4\text{S}_3 \text{ (s,l,g)}$
249	PHOSPHORYL TRICHLORIDE	$\text{POCl}_3 \text{ (g)}$
250	PORTLANDITE	$\text{CaO}_2\text{H}_2 \text{ (s,g)}$
251	POTASSIUM	K (s,l,g)
252	POTASSIUM	$\text{K}_2 \text{ (g)}$
253	POTASSIUM ALUMINUM SULFATE	$\text{KAlS}_2\text{O}_8 \text{ (s)}$
254	POTASSIUM CARBONATE	$\text{K}_2\text{CO}_3 \text{ (s,l)}$
255	POTASSIUM CHLORIDE	KCl (s,l,g)
256	POTASSIUM CYANIDE	KCN (s,l,g)
257	POTASSIUM DIOXIDE	$\text{KO}_2 \text{ (s)}$
258	POTASSIUM HEXACHLOROALUMINATE	$\text{K}_3\text{AlCl}_6 \text{ (s)}$
259	POTASSIUM HYDRIDE	KH (s,g)
260	POTASSIUM HYDROXIDE	KOH (s,l,g)
261	POTASSIUM MONOXIDE	KO (g)
262	POTASSIUM NANOCHLOROALUMINATE	$\text{K}_3\text{Al}_2\text{Cl}_7 \text{ (s)}$
263	POTASSIUM OXIDE	$\text{K}_2\text{O (s)}$
264	POTASSIUM PERCHLORATE	$\text{KClO}_4 \text{ (s)}$
265	POTASSIUM PEROXIDE	$\text{K}_2\text{O}_2 \text{ (s)}$
266	POTASSIUM SILICATE	$\text{K}_2\text{SiO}_3 \text{ (s,l)}$
267	POTASSIUM SULFATE	$\text{K}_2\text{SO}_4 \text{ (s,l,g)}$
268	POTASSIUM SULFIDE	$\text{K}_2\text{S (s,l)}$
269	POTASSIUM TETRACHLOROALUMINATE	$\text{KAlCl}_4 \text{ (s)}$

FEF DATABASE

Chemical
Name Index

No.	Name	Formula
270	PYRITE	FeS_2 (s)
271	PYROPE	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (s)
272	PYROPHYLLITE	$\text{Al}_2\text{Si}_4\text{H}_2\text{O}_{12}$ (s)
273	PYRRHOTITE	$\text{Fe}_{0.877}\text{S}$ (s)
274	RUTILE	TiO_2 (s,l,g)
275	SILICON	Si (s,l,g)
276	SILICON	Si_2 (g)
277	SILICON	Si_3 (g)
278	SILICON CARBIDE	SiC (s,g)
279	SILICON DICARBIDE	SiC_2 (g)
280	SILICON DICHLORIDE	SiCl_2 (g)
281	SILICON DIOXIDE	SiO_2 (s,l,g)
282	SILICON DISULFIDE	SiS_2 (s,l)
283	SILICON HYDRIDE	SiH (g)
284	SILICON MONOCHLORIDE	SiCl (g)
285	SILICON MONOXIDE	SiO (g)
286	SILICON NITRIDE	SiN (g)
287	SILICON SULFIDE	SiS (g)
288	SILICON TETRACHLORIDE	SiCl_4 (g)
289	SILICON TETRAHYDRIDE	SiH_4 (g)
290	SILICON TRICHLORIDE	SiCl_3 (g)
291	SODIUM	Na (s,l,g)
292	SODIUM	Na_2 (g)
293	SODIUM ALUMINATE	NaAlO_2 (s)
294	SODIUM CARBONATE	Na_2CO_3 (s,l)
295	SODIUM CHLORIDE	NaCl (s,l,g)
296	SODIUM CYANIDE	NaCN (s,l,g)
297	SODIUM DIOXIDE	NaO_2 (s)
298	SODIUM DISILICATE	$\text{Na}_2\text{Si}_2\text{O}_5$ (s,l)
299	SODIUM DISULFIDE	Na_2S_2 (s,l)
300	SODIUM HEXACHLOROALUMINATE	Na_3AlCl_6 (s)
301	SODIUM HYDRIDE	NaH (s,g)
302	SODIUM HYDROXIDE	NaOH (s,l,g)
303	SODIUM MONOXIDE	NaO (g)
304	SODIUM OXIDE	Na_2O (s,l)
305	SODIUM PERCHLORATE	NaClO_4 (s)
306	SODIUM PEROXIDE	Na_2O_2 (s)
307	SODIUM SILICATE	Na_2SiO_3 (s,l)
308	SODIUM SULFATE	Na_2SO_4 (s,l,g)
309	SODIUM SULFIDE	Na_2S (s,l)
310	SODIUM TETRACHLOROALUMINATE	NaAlCl_4 (s)
311	SPINEL	MgAl_2O_4 (s,l)
312	SULFUR	S (s,l,g)
313	SULFUR	S_2 (g)
314	SULFUR	S_8 (g)

FEF DATABASE

Chemical
Name Index

No.	Name	Formula
315	SULFUR	S ₄ (g)
316	SULFUR	S ₅ (g)
317	SULFUR	S ₆ (g)
318	SULFUR	S ₇ (g)
319	SULFUR	S ₈ (g)
320	SULFUR DICHLORIDE	SCl ₂ (l,g)
321	SULFUR DIOXIDE	SO ₂ (g)
322	SULFUR MONOCHLORIDE	SCl (g)
323	SULFUR MONOXIDE	SO (g)
324	SULFUR NITRIDE	SN (g)
325	SULFUR TRIOXIDE	SO ₃ (g)
326	SULFURIC ACID	H ₂ SO ₄ (l,g)
327	SULFURIC ACID DIHYDRATE	H ₄ SO ₆ (l)
328	SULFURIC ACID HEMIHEXAHYDRATE	H ₁₅ SO _{10.500} (l)
329	SULFURIC ACID MONOHYDRATE	H ₄ SO ₅ (l)
330	SULFURIC ACID TETRAHYDRATE	H ₁₀ SO ₈ (l)
331	SULFURIC ACID TRIHYDRATE	H ₈ SO ₇ (l)
332	SULFURYL CHLORIDE	SO ₂ Cl ₂ (g)
333	TETRACHLOROETHYLENE	C ₂ Cl ₄ (g)
334	TETRAMETHYLSILANE	SiC ₄ H ₁₂ (g)
335	THIOPHOSPHORYL TRICHLORIDE	SPCl ₃ (g)
336	TITANITE (SPHENE)	CaTiSiO ₅ (s)
337	TITANIUM	Ti (s,l,g)
338	TITANIUM CARBIDE	TiC (s,l)
339	TITANIUM DICHLORIDE	TiCl ₂ (s,g)
340	TITANIUM HYDRIDE	TiH ₂ (s)
341	TITANIUM HYPOCHLORATE	TiOCl ₂ (g)
342	TITANIUM HYPOCHLORITE	TiOCl (g)
343	TITANIUM MONOCHLORIDE	TiCl (s)
344	TITANIUM MONOXIDE	TiO (s,l,g)
345	TITANIUM NITRIDE	TiN (s,l)
346	TITANIUM OXIDE	Ti ₂ O ₃ (s,l)
347	TITANIUM PENTAOXIDE	Ti ₅ O ₅ (s,l)
348	TITANIUM SEPTOXIDE	Ti ₄ O ₇ (s,l)
349	TITANIUM TETRACHLORIDE	TiCl ₄ (s,l,g)
350	TITANIUM TRICHLORIDE	TiCl ₃ (s,g)
351	TREMOLITE	Ca ₂ Mg ₅ Si ₈ H ₂ O ₂₄ (s)
352	TRICHLOROMETHANE	CHCl ₃ (g)
353	TRICHLOROMETHYL	CCl ₃ (g)
354	TRICHLOROMETHYLSILANE	SiCH ₃ Cl ₃ (g)
355	TRICHLOROSILANE	SiHCl ₃ (g)
356	TRICOPPER TRICHLORIDE	Cu ₃ Cl ₃ (g)
357	TRIHYDROGEN PHOSPHIDE	H ₃ P (g)
358	TRILITHIUM NITRIDE	Li ₃ N (s)
359	TRILITHIUM TRICHLORIDE	Li ₃ Cl ₃ (g)

FEF DATABASE

**Chemical
Name Index**

No.	Name	Formula
360	TRIPHOSPHORUS PENTANITRIDE	P_3N_5 (s)
361	TRISILICON TETRANITRIDE	Si_3N_4 (s)
362	TROILITE	FeS (s,l,g)
363	WATER	H_2O (l,g)
364	WHITLOCKITE	$Ca_3P_2O_8$ (s)
365	WITHERITE	$BaCO_3$ (s)
366	WOLLASTONITE	$CaSiO_3$ (s)
367	WUSTITE	$Fe_{0.947}O$ (s)

APPENDIX B

No.	Formula	Name
0	Al	ALUMINUM (s,l,g)
1	AlC	ALUMINUM CARBIDE (g)
2	AlCl	ALUMINUM MONOCHLORIDE (g)
3	AlCl ₂	ALUMINUM DICHLORIDE (g)
4	AlCl ₃	ALUMINUM TRICHLORIDE (s,l,g)
5	AlH	ALUMINUM HYDRIDE (g)
6	AlN	ALUMINUM NITRIDE (s,g)
7	AlO	ALUMINUM MONOXIDE (g)
8	AlOCl	ALUMINUM OXYCHLORIDE (s,g)
9	AlOH	ALUMINUM HYDROXIDE (g)
10	AlO ₂	ALUMINUM DIOXIDE (g)
11	AlO ₂ H	BOEHMITE (g)
12	AlPO ₄	BERLINITE (s)
13	AlS	ALUMINUM SULFIDE (g)
14	Al ₂ Cl ₆	ALUMINUM HEXACHLORIDE (g)
15	Al ₂ O	DIALUMINUM MONOXIDE (g)
16	Al ₂ O ₂	DIALUMINUM DIOXIDE (g)
17	Al ₂ O ₃	CORUNDUM (s,l)
18	Al ₂ S ₃	ALUMINUM SULFIDE (s)
19	Al ₂ S ₃ O ₁₂	ALUMINUM SULFATE (s)
20	Al ₂ SiO ₅	ANDALUSITE (s)
21	Al ₂ Si ₄ H ₂ O ₁₂	PYROPHYLLITE (s)
22	Al ₄ C ₃	ALUMINUM TRICARBIDE (s)
23	Al ₄ Si ₂ O ₁₃	MULLITE (s,l)
24	Ar	ARGON (g)
25	Ba	BARIUM (s,l,g)
26	BaCO ₃	WITHERITE (s)
27	BaCl	BARIUM CHLORIDE (g)
28	BaCl ₂	BARIUM DICHLORIDE (s,l,g)
29	BaN ₂ O ₆	NITROBARITE (s)
30	BaO	BARIUM OXIDE (s,l,g)
31	BaOH	BARIUM MONOHYDROXIDE (g)
32	BaO ₂ H ₂	BARIUM DIHYDROXIDE (s,l,g)
33	BaS	BARIUM SULFIDE (s,g)
34	BaSO ₄	BARITE (s)
35	C	CARBON (s,g)
36	CCl	CHLOROMETHYLIDYNE (g)
37	CCl ₂	DICHLOROMETHYLENE (g)
38	CCl ₃	TRICHLOROMETHYL (g)
39	CCl ₄	CARBON TETRACHLORIDE (g)
40	CH	METHYLIDYNE (g)
41	CHCl	CHLOROMETHYLENE (g)
42	CHCl ₃	TRICHLOROMETHANE (g)
43	CHP	METHINOPHOSPHIDE (g)
44	CH ₂	METHYLENE (g)

No.	Formula	Name
45	CH ₂ Cl ₂	DICHLOROMETHANE (g)
46	CH ₂ O	FORMALDEHYDE (g)
47	CH ₃	METHYL (g)
48	CH ₃ Cl	CHLOROMETHANE (g)
49	CH ₄	METHANE (g)
50	CN	CYANOGEN (g)
51	CNCl	CYANOGEN CHLORIDE (g)
52	CO	CARBON MONOXIDE (g)
53	COCl	CARBONYL CHLORIDE (g)
54	COCl ₂	CARBONIC DICHLORIDE (g)
55	COS	CARBON OXIDE SULFIDE (g)
56	CO ₂	CARBON DIOXIDE (g)
57	CP	CARBON PHOSPHIDE (g)
58	CS	CARBON SULFIDE (g)
59	CS ₂	CARBON DISULFIDE (g)
60	C ₂	CARBON (g)
61	C ₂ Cl ₂	DICHLOROETHYNE (g)
62	C ₂ Cl ₄	TETRACHLOROETHYLENE (g)
63	C ₂ Cl ₆	HEXACHLOROETHANE (g)
64	C ₂ H	ETHYNYL (g)
65	C ₂ HCl	CHLOROETHYNE (g)
66	C ₂ H ₂	ACETYLENE (g)
67	C ₂ H ₄	ETHYLENE (g)
68	C ₂ H ₄ O	OXIRANE (g)
69	C ₂ N ₂	ETHANEDINITRILE (g)
70	C ₃	CARBON (g)
71	C ₃ O ₂	CARBON SUBOXIDE (g)
72	C ₄	CARBON (g)
73	C ₄ N ₂	2-BUTYNEDINITRILE (g)
74	C ₅	CARBON (g)
75	Ca	CALCIUM (s,l,g)
76	CaAl ₂ SiO ₆	CA-AL PYROXENE (s)
77	CaAl ₂ Si ₂ O ₈	ANORTHITE (s,l)
78	CaCO ₃	CALCITE (s)
79	CaCl	CALCIUM MONOCHLORIDE (g)
80	CaCl ₂	HYDROPHILITE (s,l,g)
81	CaFe ₂ O ₄	CALCIUM FERRITE (s)
82	CaMgC ₂ O ₄	DOLOMITÉ (s)
83	CaMgSi ₂ O ₆	DIOPSIDE (s,l)
84	CaN ₂ O ₆	CALCIUM NITRATE (s)
85	CaO	CALCIUM OXIDE (s,l,g)
86	CaOH	CALCIUM MONOHYDROXIDE (g)
87	CaO ₂ H ₂	PORTLANDITE (s,g)
88	CaS	OLDHAMITE (s,g)
89	CaSO ₄	ANHYDRITE (s)

FEF DATABASE

Chemical
Formula Index

No.	Formula	Name
90	CaSiO_3	WOLLASTONITE (s)
91	CaTiO_3	PEROVSKITE (s)
92	CaTiSiO_5	TITANITE (SPHENE) (s)
93	$\text{Ca}_2\text{Al}_2\text{SiO}_7$	GEHLENITE (s,l)
94	$\text{Ca}_2\text{Fe}_2\text{O}_5$	DICALCIUM FERRITE (s)
95	$\text{Ca}_2\text{MgSi}_2\text{O}_7$	AKERMANITE (s)
96	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{H}_2\text{O}_{24}$	TREMOLITE (s)
97	Ca_2SiO_4	LARNITE (CA-OLIVINE) (s)
98	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	GROSSULAR (s)
99	$\text{Ca}_3\text{MgSi}_2\text{O}_8$	MERWINITE (s)
100	$\text{Ca}_3\text{P}_2\text{O}_8$	WHITLOCKITE (s)
101	$\text{Ca}_5\text{F}_3\text{HO}_{13}$	HYDROXYAPATITE (s)
102	Cl	CHLORINE (g)
103	ClO	CHLORINE MONOXIDE (g)
104	ClO ₂	CHLORINE DIOXIDE (g)
105	Cl ₂	CHLORINE (g)
106	Cl ₂ O	DICHLORINE MONOXIDE (g)
107	Cu	COPPER (s,l,g)
108	CuCN	COPPER CYANIDE (s)
109	CuCl	COPPER MONOCHLORIDE (s,l,g)
110	CuCl ₂	COPPER DICHLORIDE (s)
111	CuH_2O_2	COPPER HYDROXIDE (s)
112	CuO	COPPER OXIDE (s,g)
113	CuSO_4	COPPER SULFATE (s)
114	Cu ₂	COPPER (g)
115	Cu ₂ O	CUPROUS OXIDE (s,l)
116	Cu ₂ S	CHALCOCITE (s)
117	Cu_2SO_5	DICOPPER SULFATE (s)
118	Cu_3Cl_3	TRICOPPER TRICHLORIDE (g)
119	$\text{Fe}_{0.877}\text{S}$	PYRRHOTITE (s)
120	$\text{Fe}_{0.947}\text{O}$	WUSTITE (s)
121	Fe	IRON (s,l,g)
122	FeC_5O_5	IRON CARBONYL (l,g)
123	FeCl	IRON MONOCHLORIDE (g)
124	FeCl ₂	IRON DICHLORIDE (s,l,g)
125	FeCl ₃	IRON TRICHLORIDE (s,l,g)
126	FeH_2O_2	IRON HYDROXIDE (s,g)
127	FeH_3O_3	IRON TRIHYDROXIDE (s)
128	FeO	IRON OXIDE (s,l,g)
129	FeS	TROILITE (s,l,g)
130	FeSO_4	IRON SULFATE (s)
131	FeS ₂	PYRITE (s)
132	FeTiO_3	ILMENITE (s)
133	Fe_2Cl_4	DIIRON TETRACHLORIDE (g)
134	Fe_2Cl_6	DIIRON HEXACHLORIDE (g)

No.	Formula	Name
135	Fe_2O_3	HEMATITE (s)
136	$\text{Fe}_2\text{S}_3\text{O}_{12}$	FERRIC SULFATE (s)
137	Fe_2SiO_4	FAYALITE (s)
138	Fe_3C	COHENITE (s)
139	Fe_3O_4	MAGNETITE (s)
140	H	HYDROGEN (g)
141	HCN	HYDROGEN CYANIDE (g)
142	HCNO	HYDROGEN ISOCYANATE (g)
143	HCO	FORMYL (g)
144	HCl	HYDROGEN CHLORIDE (g)
145	HNO	NITROXYL (g)
146	HNO_2	NITROUS ACID (g)
147	HNO_3	NITRIC ACID (g)
148	HOCl	HYPOCHLOROUS ACID (g)
149	HO_2	HYDROPEROXO (g)
150	HP	HYDROGEN PHOSPHIDE (g)
151	HS	MERCAPTO (g)
152	H_2	HYDROGEN (g)
153	H_2O	WATER (l,g)
154	H_2O_2	HYDROGEN PEROXIDE (g)
155	H_2P	DIHYDROGEN PHOSPHIDE (g)
156	H_2S	HYDROGEN SULFIDE (g)
157	H_2SO_4	SULFURIC ACID (l,g)
158	H_3P	TRIHYDROGEN PHOSPHIDE (g)
159	H_3PO_4	PHOSPHORIC ACID (s,l)
160	H_4SO_5	SULFURIC ACID MONOHYDRATE (l)
161	H_4SO_6	SULFURIC ACID DIHYDRATE (l)
162	H_6SO_7	SULFURIC ACID TRIHYDRATE (l)
163	H_{10}SO_8	SULFURIC ACID TETRAHYDRATE (l)
164	$\text{H}_{15}\text{SO}_{10.500}$	SULFURIC ACID HEMIHEXAHYDRATE (l)
165	K	POTASSIUM (s,l,g)
166	KAlCl_4	POTASSIUM TETRACHLOROALUMINATE (s)
167	KAlS_2O_8	POTASSIUM ALUMINUM SULFATE (s)
168	KAlSiO_4	KALIOPHILLITE (s)
169	KAlSi_2O_6	LEUCITE (s)
170	KAlSi_3O_8	HIGH SANIDINE (s,l)
171	$\text{KAl}_3\text{Si}_3\text{H}_2\text{O}_{12}$	MUSCOVITE (s)
172	KCN	POTASSIUM CYANIDE (s,l,g)
173	KCl	POTASSIUM CHLORIDE (s,l,g)
174	KClO_4	POTASSIUM PERCHLORATE (s)
175	KH	POTASSIUM HYDRIDE (s,g)
176	KNO_3	NITER (s)
177	KO	POTASSIUM MONOXIDE (g)
178	KOH	POTASSIUM HYDROXIDE (s,l,g)
179	KO_2	POTASSIUM DIOXIDE (s)

No.	Formula	Name
180	K ₂	POTASSIUM (g)
181	K ₂ CO ₃	POTASSIUM CARBONATE (s,l)
182	K ₂ C ₂ N ₂	DIPOTASSIUM CYANIDE (g)
183	K ₂ Cl ₂	DIPOTASSIUM DICHLORIDE (g)
184	K ₂ H ₂ O ₂	DIPOTASSIUM DIHYDROXIDE (g)
185	K ₂ O	POTASSIUM OXIDE (s)
186	K ₂ O ₂	POTASSIUM PEROXIDE (s)
187	K ₂ S	POTASSIUM SULFIDE (s,l)
188	K ₂ SO ₄	POTASSIUM SULFATE (s,l,g)
189	K ₂ SiO ₃	POTASSIUM SILICATE (s,l)
190	K ₃ AlCl ₆	POTASSIUM HEXACHLOROALUMINATE (s)
191	K ₃ Al ₂ Cl ₇	POTASSIUM NANOCHLOROALUMINATE (s)
192	Li	LITHIUM (s,l,g)
193	LiAlH ₄	LITHIUM TETRAHYDROALUMINATE (s)
194	LiAlO ₂	LITHIUM ALUMINATE (s,l)
195	LiCl	LITHIUM MONOCHLORIDE (s,l,g)
196	LiClO ₄	LITHIUM PERCHLORATE (s,l)
197	LiH	LITHIUM HYDRIDE (s,l,g)
198	LiN	LITHIUM NITRIDE (g)
199	LiNaO	LITHIUM SODIUM OXIDE (g)
200	LiO	LITHIUM MONOXIDE (g)
201	LiOCl	LITHIUM HYPOCHLORITE (g)
202	LiOH	LITHIUM HYDROXIDE (s,l,g)
203	LiON	LITHIUM OXYNITRIDE (g)
204	Li ₂	LITHIUM (g)
205	Li ₂ CO ₃	LITHIUM CARBONATE (s,l)
206	Li ₂ C ₂	LITHIUM CARBIDE (s)
207	Li ₂ Cl ₂	DILITHIUM DICHLORIDE (g)
208	Li ₂ H ₂ O ₂	DILITHIUM DIHYDROXIDE (g)
209	Li ₂ O	LITHIUM OXIDE (s,l,g)
210	Li ₂ O ₂	LITHIUM PEROXIDE (s,g)
211	Li ₂ SO ₄	LITHIUM SULFATE (s,l,g)
212	Li ₂ SiO ₃	LITHIUM SILICATE (s,l)
213	Li ₂ Si ₂ O ₅	LITHIUM DISILICATE (s,l)
214	Li ₂ TiO ₃	LITHIUM TITANATE (s,l)
215	Li ₃ Cl ₃	TRILITHIUM TRICHLORIDE (g)
216	Li ₃ N	TRILITHIUM NITRIDE (s)
217	Mg	MAGNESIUM (s,l,g)
218	MgAl ₂ O ₄	SPINEL (s,l)
219	MgCO ₃	MAGNESITE (s)
220	MgC ₂	MAGNESIUM CARBIDE (s)
221	MgCl	MAGNESIUM MONOCHLORIDE (g)
222	MgCl ₂	MAGNESIUM DICHLORIDE (s,l,g)
223	MgFe ₂ O ₄	MAGNESIOFERRITE (s)
224	MgH	MAGNESIUM HYDRIDE (g)

No.	Formula	Name
225	MgH ₂	MAGNESIUM DIHYDRIDE (s)
226	MgH ₂ O ₂	MAGNESIUM DIHYDROXIDE (s,g)
227	MgN	MAGNESIUM NITRIDE (g)
228	MgN ₂ O ₄	MAGNESIUM NITRATE (s)
229	MgO	MAGNESIUM OXIDE (s,l,g)
230	MgOH	MAGNESIUM HYDROXIDE (g)
231	MgS	MAGNESIUM SULFIDE (s,g)
232	MgSO ₄	MAGNESIUM SULFATE (s,l)
233	MgSiO ₃	MAGNESIUM SILICATE (s,l)
234	MgTiO ₃	MAGNESIUM TITANATE (s,l)
235	MgTi ₂ O ₅	MAGNESIUM DITITANATE (s,l)
236	Mg ₂	MAGNESIUM (g)
237	Mg ₂ Al ₄ Si ₅ O ₁₈	CORDIERITE (s)
238	Mg ₂ C ₃	MAGNESIUM CARBIDE (s)
239	Mg ₂ Cl ₄	DIMAGNESIUM TETRACHLORIDE (g)
240	Mg ₂ Si	MAGNESIUM SILICIDE (s,l)
241	Mg ₂ SiO ₄	FORSTERITE (s,l)
242	Mg ₂ TiO ₄	MAGNESIUM ORTHOTITANATE (s,l)
243	Mg ₃ Al ₂ Si ₃ O ₁₂	PYROPE (s)
244	Mg ₃ N ₂	MAGNESIUM DINITRIDE (s)
245	Mg ₃ P ₂ O ₈	MAGNESIUM PHOSPHATE (s,l)
246	N	NITROGEN (g)
247	NH	IMIDOGEN (g)
248	NH ₂	AMIDOGEN (g)
249	NH ₃	AMMONIA (g)
250	NH ₄ Cl	AMMONIUM CHLORIDE (s)
251	NH ₄ ClO ₄	AMMONIUM PERCHLORATE (s)
252	NO	NITROGEN MONOXIDE (g)
253	NOCl	NITROSYL CHLORIDE (g)
254	NO ₂	NITROGEN DIOXIDE (g)
255	NO ₂ Cl	NITRYL CHLORIDE (g)
256	NO ₃	NITROGEN TRIOXIDE (g)
257	N ₂	NITROGEN (g)
258	N ₂ H ₂	DIAZENE (CIS) (g)
259	N ₂ H ₄	HYDRAZINE (l,g)
260	N ₂ H ₄ O ₃	AMMONIUM NITRATE (s)
261	N ₂ H ₆ SO ₄	MASCAGNITE (s)
262	N ₂ O	DINITROGEN OXIDE (g)
263	N ₂ O ₃	DINITROGEN TRIOXIDE (g)
264	N ₂ O ₄	DINITROGEN TETRAOXIDE (s,l,g)
265	N ₂ O ₅	DINITROGEN PENTAOXIDE (g)
266	N ₃	AZIDE (g)
267	Na	SODIUM (s,l,g)
268	NaAlCl ₄	SODIUM TETRACHLOROALUMINATE (s)
269	NaAlO ₂	SODIUM ALUMINATE (s)

No.	Formula	Name
270	NaAlSiO ₄	NEPHELINE (s,l)
271	NaAlSi ₂ O ₆	JADEITE (s,l)
272	NaAlSi ₃ O ₈	ALBITE (s,l)
273	NaCN	SODIUM CYANIDE (s,l,g)
274	NaCl	SODIUM CHLORIDE (s,l,g)
275	NaClO ₄	SODIUM PERCHLORATE (s)
276	NaH	SODIUM HYDRIDE (s,g)
277	NaO	SODIUM MONOXIDE (g)
278	NaOH	SODIUM HYDROXIDE (s,l,g)
279	NaO ₂	SODIUM DIOXIDE (s)
280	Na ₂	SODIUM (g)
281	Na ₂ CO ₃	SODIUM CARBONATE (s,l)
282	Na ₂ C ₂ N ₂	DISODIUM CYANIDE (g)
283	Na ₂ Cl ₂	DISODIUM DICHLORIDE (g)
284	Na ₂ H ₂ O ₂	DISODIUM DIHYDROXIDE (g)
285	Na ₂ O	SODIUM OXIDE (s,l)
286	Na ₂ O ₂	SODIUM PEROXIDE (s)
287	Na ₂ S	SODIUM SULFIDE (s,l)
288	Na ₂ SO ₄	SODIUM SULFATE (s,l,g)
289	Na ₂ S ₂	SODIUM DISULFIDE (s,l)
290	Na ₂ SiO ₃	SODIUM SILICATE (s,l)
291	Na ₂ Si ₂ O ₅	SODIUM DISILICATE (s,l)
292	Na ₃ AlCl ₄	SODIUM HEXACHLOROALUMINATE (s)
293	O	OXYGEN (g)
294	O ₂	OXYGEN (g)
295	O ₃	OZONE (g)
296	P	PHOSPHORUS (s,l,g)
297	PCl	PHOSPHOROUS MONOCHLORIDE (g)
298	PCl ₃	PHOSPHORUS TRICHLORIDE (g)
299	PCl ₅	PHOSPHORUS PENTACHLORIDE (g)
300	PN	PHOSPHORUS NITRIDE (g)
301	PO	PHOSPHORUS MONOXIDE (g)
302	POCl ₃	PHOSPHORYL TRICHLORIDE (g)
303	PO ₂	PHOSPHORUS DIOXIDE (g)
304	PS	PHOSPHORUS SULFIDE (g)
305	P ₂	PHOSPHORUS (g)
306	P ₂ N ₅	TRIPHOSPHORUS PENTANITRIDE (s)
307	P ₄	PHOSPHORUS (g)
308	P ₄ O ₆	PHOSPHORUS TRIOXIDE DIMER (g)
309	P ₄ O ₁₀	PHOSPHORUS PENTAOXIDE DIMER (s,g)
310	P ₄ S ₃	PHOSPHORUS TRISULFIDE (s,l,g)
311	S	SULFUR (s,l,g)
312	SCl	SULFUR MONOCHLORIDE (g)
313	SCl ₂	SULFUR DICHLORIDE (l,g)
314	SN	SULFUR NITRIDE (g)

No.	Formula	Name
315	SO	SULFUR MONOXIDE (g)
316	SO ₂	SULFUR DIOXIDE (g)
317	SO ₂ Cl ₂	SULFURYL CHLORIDE (g)
318	SO ₃	SULFUR TRIOXIDE (g)
319	SPOCl ₃	THIOPHOSPHORYL TRICHLORIDE (g)
320	S ₂	SULFUR (g)
321	S ₂ Cl	DISULFUR MONOCHLORIDE (g)
322	S ₂ Cl ₂	DISULFUR DICHLORIDE (l,g)
323	S ₂ O	DISULFUR MONOXIDE (g)
324	S ₃	SULFUR (g)
325	S ₄	SULFUR (g)
326	S ₅	SULFUR (g)
327	S ₆	SULFUR (g)
328	S ₇	SULFUR (g)
329	S ₈	SULFUR (g)
330	Si	SILICON (s,l,g)
331	SiC	SILICON CARBIDE (s,g)
332	SiCH ₃ Cl ₃	TRICHLOROMETHYLSILANE (g)
333	SiC ₂	SILICON DICARBIDE (g)
334	SiC ₄ H ₁₂	TETRAMETHYLSILANE (g)
335	SiCl	SILICON MONOCHLORIDE (g)
336	SiCl ₂	SILICON DICHLORIDE (g)
337	SiCl ₃	SILICON TRICHLORIDE (g)
338	SiCl ₄	SILICON TETRACHLORIDE (g)
339	SiH	SILICON HYDRIDE (g)
340	SiHCl ₃	TRICHLOROSILANE (g)
341	SiH ₂ Cl ₂	DICHLOROSILANE (g)
342	SiH ₃ Cl	CHLOROSILANE (g)
343	SiH ₄	SILICON TETRAHYDRIDE (g)
344	SiN	SILICON NITRIDE (g)
345	SiO	SILICON MONOXIDE (g)
346	SiO ₂	SILICON DIOXIDE (s,l,g)
347	SiS	SILICON SULFIDE (g)
348	SiS ₂	SILICON DISULFIDE (s,l)
349	Si ₂	SILICON (g)
350	Si ₂ N	DISILICON NITRIDE (g)
351	Si ₃	SILICON (g)
352	Si ₃ N ₄	TRISILICON TETRANITRIDE (s)
353	Ti	TITANIUM (s,l,g)
354	TiC	TITANIUM CARBIDE (s,l)
355	TiCl	TITANIUM MONOCHLORIDE (s)
356	TiCl ₂	TITANIUM DICHLORIDE (s,g)
357	TiCl ₃	TITANIUM TRICHLORIDE (s,g)
358	TiCl ₄	TITANIUM TETRACHLORIDE (s,l,g)
359	TiH ₂	TITANIUM HYDRIDE (s)

No.	Formula	Name
360	TiN	TITANIUM NITRIDE (s,l)
361	TiO	TITANIUM MONOXIDE (s,l,g)
362	TiOCl	TITANIUM HYPOCHLORITE (g)
363	TiOCl ₂	TITANIUM HYPOCHLORATE (g)
364	TiO ₂	RUTILE (s,l,g)
365	Ti ₂ O ₃	TITANIUM OXIDE (s,l)
366	Ti ₃ O ₅	TITANIUM PENTAOXIDE (s,l)
367	Ti ₄ O ₇	TITANIUM SEPTOXIDE (s,l)

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Hot-Gas Cleanup (2.4)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-86
		6. Completion Date 9-30-92

7. FY 91/92	8. Months or Quarters Quarters	1991 JUL AUG SEP OCT NOV DEC						1992 JAN FEB MAR APR MAY JUN								
9. Cost Status	a. Dollars Expressed in Thousands	b. Dollar Scale														
10. Cost Chart																
Fund Source			Quarter				Cum. to Date		Tot. Plan							
			1st	2nd	3rd	4th										
DOE			P 88	87	88	87	350	350								
			A 32	86	75	123	296									
			P													
			A													
			P													
			A													
			P													
			A													
Total P			88	87	88	87	350	350								
Total A			32	86	75	123	296									
Variance			56	21	13	(36)	54									
P = Planned A = Actual																
Total Planned Costs for Program/Project \$350			Planned		88		175		263		350					
			Actual		32		98		173		296					
			Variance		56		77		90		54					

11. Major Milestone Status	Units Planned	Units Complete
A. Literature Review	P	C
		No activities in current project year.
	P	C
B. Hot-Gas Particulate Control	P	C
		2 3
	P	C
C. Hot-Gas Sulfur Control	P	C
		No activities in current project year.
	P	C
D. Alkali Transformation and Interaction Studies	P	C
		1 2 3 4
	P	C
E. Semiannual Project Reports	P	C
		1 2
	P	C
	P	C
	P	C
	P	C
	P	C
	P	C
	P	C
	P	C
	P	C
	P	C
	P	C

12. Remarks Due to the EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.
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13. Signature of Recipient and Date	14. Signature of DOE Reviewing Representative and Date
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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Hot-Gas Cleanup (2.4)		3. Reporting Period 4-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task B	Hot-Gas Particulate Control:			Task deleted.	
b.1	Operational tests on HTHP cyclone	11-1-91			
b.2	Modify sampling equipment	4-1-92			
b.3	Modify hot-gas test loop	10-1-92			
Task D	Alkali Transformation and Interaction Studies:				
d.1	Improve PHOEBE data base	11-1-91	11-1-91		
d.2	Run simulations	2-1-92	3-31-92		
d.3	Perform gettering experiments	3-1-92	5-31-92		
d.4	Perform ceramic protection experiments	6-30-92			
Task E	Semiannual Project Reports:				
e.1	First-half report	1-15-92			
e.2	Second-half report	6-30-92			

3.0 ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT

3.1 Turbine Combustion Phenomena

TURBINE COMBUSTION PHENOMENA

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

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TURBINE COMBUSTION PHENOMENA

1.0 INTRODUCTION

Under DOE sponsorship coal-water slurry fuels have been investigated as fuels for gas turbine engines for several years, but the major technical problems still inhibiting commercialization are deposits on the pressure and suction sides of the turbine blades which reduce the gas flow area and turbine efficiency; acceptable coal burnout, given the short residence time inherent with gas turbine engines; corrosion of turbine blades by condensed alkali sulfates; erosion of turbine blades and other components by ash particles entrained in the products of combustion; and control of NO_x , SO_2 , and particulate emissions. The release of certain mineral matter species found in both raw and beneficiated coals can lead to ash deposition on surfaces, regardless of the ash content of the fuel. This deposition can lead to corrosion on and metal loss of critical turbine components and, ultimately, to derating, unavailability, or catastrophic failure of the power generation system. Alkali metals and sulfur, existing as impurities in coal, have been identified as key components in the initiation of deposition and the onset of corrosion.

Until the last six years, low-rank coals (LRCs) were not considered as potential fuels for gas turbine engines because of their high intrinsic moisture levels. It is extremely difficult to prepare a pumpable slurry of as-mined lignite with a dry solids loading over 35 wt% due to the high moisture levels in LRCs. However, with the advent of the University of North Dakota's Energy and Environmental Research Center's (EERC's) hydrothermal treatment process, micronized lignite slurries have been produced with a solids loading up to 50% and a heating value over 6000 Btu per pound of slurry (1,2). Subbituminous coals also respond very well to hydrothermal treatment and produce higher quality slurries. Availability of a slurry with a high enough fuel value to sustain combustion makes it possible to take advantage of the desirable characteristics of low-rank coals, namely, the higher reactivity of its nonvolatile carbonaceous components. Thus a low-rank coal slurry should require less residence time in the gas turbine combustor for complete combustion or, inversely, the coal would not have to be micronized as finely to achieve >99% burnout, thereby reducing fuel preparation costs. Estimates of the process have indicated that a minemouth process plant in the Powder River Basin can produce a LRCWF at around \$1.50/MM Btu, including coal costs (3). Another potential advantage of low-rank coal slurries is their nonagglomerating tendency relative to bituminous slurries, reducing the importance of atomization to very fine droplet sizes.

During the Turbine Combustion Phenomena project, seventeen successful combustion tests using CWF were completed. These tests included seven tests with a commercially available Otisca Industries-produced, Taggart seam bituminous fuel and five tests each with physically and chemically cleaned Beulah-Zap lignite and a chemically cleaned Kemmerer subbituminous fuel. Analyses of the emission and fly ash samples highlighted the superior burnout experienced by the LRCWFS as compared to the bituminous fuel even under a longer residence time profile for the bituminous fuel. While the LRC fuels are experiencing better burnout than the bituminous fuels, it is possible that differences in slurry rheology (and, therefore, in atomization) might account for some of the difference in the observed burnout rather than differences in

fuel reactivity. The LRC fly ash showed a decrease in particle size as compared to the starting fuel, while the bituminous fuel showed an increase in particle size as compared to the starting fuel. These particle-size analyses provide some evidence of low-rank coals' nonagglomerating properties as compared to bituminous fuels.

Statistical analysis of the carbon burnout data generated in a series of parametric combustion tests generated simple models to predict the carbon burnout achievable under a given range of operating conditions. These models indicate that fuel type has a significant effect on the measured carbon burnout. The LRC fuels have high carbon burnouts (97.5% to 98.7%) and appear to be relatively unaffected by other operating parameters; however, the bituminous fuel was significantly affected by combustion air temperature, atomizing air-to-fuel ratio, and fuel firing rate. In this model, bituminous fuel carbon burnouts comparable to those of the LRC fuels can be achieved, but only under the most optimum conditions.

As might be expected with the relatively high ash in the LRC fuels and lower ash fusion temperatures, significant ash deposition and slagging occurred in the turbine simulator. The XRD analysis suggests that the residual magnetite left from the physical cleaning process remains as magnetite in the reducing atmosphere of the rich zone, but is converted to hematite when it reaches the highly oxidizing atmosphere encountered in the lean combustion zone. The composition of the constituents in the ash does not indicate the preferential deposition of any component in a single area of the turbine. Material balances indicate that the Beulah Zap lignite fuel had a much higher deposition potential as demonstrated by high levels (approximately 70 wt%) of ash recovered in the combustor. The Kemmerer fuel also showed higher deposition levels than the Otisca fuel, with approximately 12-13 wt% of the ash being retained in the combustor. With the Otisca fuel combustion tests approximately 8 wt% of the ash was retained in the combustor, while over 40 wt% of the Otisca fly ash was recovered in the cyclone pot. This is probably the result of the cyclone ash containing high levels of carbon (60% or greater); thus a large percentage of the fine mineral grains is still tied up in the char cenospheres and has not been released from the char particle where it could contact internal surfaces to form deposits.

2.0 GOALS AND OBJECTIVES

The overall objective of this research is to continue to expand the database on the effects of low-rank coals' unique properties on their combustion behavior in pressurized combustion systems, such as gas turbine engines. Research will be directed toward understanding the properties of LRC fuels which affect ignition and burn times, combustion efficiency, vaporization and deposition of inorganics, and the erosion of critical gas turbine components. Special emphasis will be placed on an investigation of LRC high-shear rheology and its effect on atomization and combustion behavior, an evaluation of LRCs' nonagglomerating properties, an investigation of particulate hot-gas cleanup techniques, and inorganic transformations/alkali vaporization using a pressurized drop-tube furnace.

2.1 Three-Year Project Objectives

- Task A Revise Technology and Market Assessment. This literature review will enable EERC personnel to assess the current status of coal-fired gas turbine research to determine what recent advances have been made by other researchers. This effort will build upon the technology and market assessment made at the start of this program. This task is to be performed in Year Four.
- Task B Characterization of LRCs' Atomization Properties. This task will examine the pressurized atomization characteristics of recently produced LRC fuels with a Malvern 2600 particle-size analyzer and still photography in a pressurized spray chamber constructed at the EERC. The combustion behavior of the previous fuels tested in the spray chamber and new fuels produced for the turbine project will be evaluated under similar air-to-fuel and pressure ratios in the gas turbine simulator. This task will also look at different atomizer types in a effort to minimize spray droplet size distributions and increase combustion performance for a given rheology and atomizing air-to-fuel ratio.
- Task C Evaluation of LRC Fuel Agglomeration. The objective of this task is to evaluate the agglomerating or nonagglomerating tendencies of LRC fuels by providing optical access for an Insitex particle counter, sizer, and velocimeter (PCSV) at various positions along the axis of a pressurized drop-tube furnace recently constructed at the EERC. Thus products of combustion (POC) particle-size distributions as a function of residence time and the starting particle-size distribution and droplet size can be measured to determine if the smaller particle-size distributions found in the LRC fly ash are the result of a gradual burnout of slurry droplet agglomerates or the result of agglomerate disintegration into its original particle-size distribution due to the high thermal friability of LRC fuels.
- Task D Investigation of Particulate Hot-Gas Cleanup Systems. The objective of this task is to evaluate potential hot-gas particulate cleanup techniques as to their relative probability of success and test the best two or three systems in the turbine simulator. This task will include a technology assessment that will build upon a previous literature search performed on hot-gas cleanup techniques. These techniques could include, but would not be limited to, ceramic cross-flow filters and filter candles, nested fiber filters, cyclones, and HTHP Electrostatic precipitators (ESPs). The HTHP cyclone work started in Year Four will be continued in the Year Five Hot-Gas Cleanup program. This work involves tests with various CWFs' in an the effort to reduce the fly ash particle-size distribution entering the deposition section of the turbine simulator to 95% less than 5 microns in order to limit the amount of particle impaction on the turbine blades.
- Task E Ash Transformation Studies. The objective of this task is to investigate the ash transformations experienced by mineral matter in beneficiated low-rank coal fuels. Very little research to date has investigated the effects of pressure and coal beneficiation on the reaction pathways taken by the mineral matter present in LRC fuels.

These transformations should be dependent on the cleaning techniques used and the level of cleaning achievable on the various coal types. Mineral matter transformations of beneficiated LRC under turbine operating conditions will be investigated in a pressurized drop-tube furnace recently constructed at the EERC. This drop-tube furnace will be capable of combusting both slurry droplets and coal particles. The effects of residence time, temperature, pressure, atmosphere, and gas/fuel flow rates can be varied to examine their effects on ash transformations and carbon burnout. The drop tube will also provide carbon burnout as a true function of residence time given the laminar gas flow. The effects of deposition probe shape and temperature and the approaching gas velocity on the measured deposition rates can also be investigated. Another advantage of the pressurized drop-tube furnace is the small quantities of fuel (up to 1.0 g/min) needed to conduct extensive deposition and burnout testing as compared to the turbine simulator (approximately 150 lb/hr). High ash fusion temperature fuels are needed under the assumption that low melting temperature ashes will stick to the cyclone wall or the ceramic material and will not be easily removed or cleaned from the hot-gas cleanup device. Technical work in this task for Year Six will consist of two tasks involving combustion tests using fuels beneficiated to various levels and fuels doped with additives selected for their ability to decrease deposition potential. These tests will measure the effect these additives have on the sticking coefficient and deposition rates measured at conditions similar to those utilized in previous deposition tests.

Task F Investigation of Slagging Combustor Design. Should concurrent beneficiation of LRC studies at the EERC indicate that acceptable ash levels and chemistry not be achievable, a vertically fired combustion zone would be built to replace the horizontally fired rich combustion zone on the current turbine simulator. This modification would enable the combustor to operate in a slagging combustor mode versus the current nonslagging combustor mode. Work on this task would be dependent on the results of the work in progress and would be subject to DOE approval.

Task G Baseline Combustion Test with Spring Creek Fuel Utilized in GM Allison Combustion Tests

The production of several barrels of minimally cleaned Spring Creek coal for the Turbine Combustion Phenomena program was added to the large production runs performed for GM Allison. A combustion test will be used to establish a performance baseline in the 1-MM Btu/hr gas turbine simulator for the Powder River Basin coal used by GM Allison in its direct coal-fired gas turbine system. Thus future comparisons of the two combustion rigs can be made, especially the performance of hot-gas cleanup devices in these systems.

2.2 Sixth-Year Objectives

Task A Revise Technology and Market Assessment

Performed in the fourth year.

Task B Characterization of LRCs' Atomization Properties

Ongoing with Year Five carryover funds.

Task C Evaluation of LRC Fuel Agglomeration

Unable to perform due to inoperability of Insitac particle sizer, counter, and velocimeter (PSCV).

Task D Investigation of Particulate Hot-Gas Cleanup Systems

The performance of long-term hot-gas cleaning tests should be performed on the PDTF (if availability permits) due to the lower cost of maintaining long test durations in this system. Parameters of interest are alkali levels, operating temperatures and pressures, particulate loading, and number of cleaning cycles.

Task E Ash Transformation Studies

Technical work in this task for Year Six will consist of two tasks involving combustion tests using fuels beneficiated to various levels and fuels doped with additives selected for their ability to increase ash fusion temperatures. These tests will measure the effect these additives have on the sticking coefficient and deposition rates measured at conditions similar to those utilized in previous deposition tests. These tests will determine an additive that hopefully will provide a fuel with a nonmolten fly ash without significantly increasing the total fly ash concentration in the flue gas. These selected doped fuels would be suitable for tests in both the HTHP cyclone and ceramic filter apparatus.

Task E-1 Ash Transformation Studies for Beneficiated LRC Fuels

The objective of this task is to investigate the ash transformations experienced by mineral matter in beneficiated low-rank coal fuels. Very little research to date has investigated the effects of pressure and coal beneficiation on the reaction pathways taken by the mineral matter present in LRC fuels. These transformations should be dependent on the cleaning techniques used and the level of cleaning achievable on the various coal types. Cleaning techniques which will be investigated are heavy media physical cleaning, an acid-leaching chemical-cleaning technique, hydrothermal treatment, and oil agglomeration. Mineral matter transformations of beneficiated LRC under turbine operating conditions will be investigated in a pressurized drop-tube furnace recently constructed at the EERC. The effects of residence time, temperature, pressure, atmosphere, and gas/fuel flow rates can be varied to examine their effects on ash transformations and carbon burnout. The drop tube will also provide carbon burnout as a true function of residence time given the laminar gas flow. The effects of deposition probe shape and temperature and the approaching gas velocity on the measured deposition rates can also be investigated.

Task E-2 PDFT Additive Testing for Improved Ash Characteristics

Alkali gettering or additives which tie up the volatile and molten species in the mineral matter is needed to protect downstream hot-gas cleanup devices and the turbine blades themselves. High ash fusion temperature fuels are needed under the assumption that low melting temperature ashes will stick to the ceramic material and will not be easily removed or cleaned from the hot-gas cleanup device. Other research needs were identified as characterizing the trace elements in the gas turbine (GT) flue gas.

Task F Investigation of Slagging Combustor Design

No technical work in this task will be performed in Year Six. If coal ash properties dictate, construction of a first-stage slagging combustor would begin in subsequent years.

Task G Baseline Combustion Test with Spring Creek Fuel Utilized in GM Allison Combustion Tests

The production of several barrels of minimally cleaned Spring Creek coal for the Turbine Combustion Phenomena program was added to the large production runs performed for GM Allison. A combustion test will be used to establish a performance baseline in the 1-MM Btu/hr gas turbine simulator for the Powder River Basin coal used by GM Allison in its direct coal-fired gas turbine system. Thus future comparisons of the two combustion rigs can be made, especially the performance of hot-gas cleanup devices in these systems.

3.0 PROJECT DESCRIPTION

3.1 One-Million Btu/Hr Gas Turbine Combustor

To meet the objectives of the initial program, a pressurized combustion vessel was built to allow the operating parameters of a direct-fired gas turbine combustor to be simulated. One goal in building this equipment was to design the gas turbine simulator as small as possible to reduce both the quantity of test fuel needed and the test fuel preparation costs, while not undersizing the combustor such that wall effects would have a significant effect on the measured combustion performance. Based on computer modeling, a rich-lean, two-stage nonslagging combustor has been constructed to simulate a direct-fired gas turbine. This design was selected to maximize the information that could be obtained on the impact of the unique properties of low-rank fuels and various hot-gas cleanup techniques on the gas turbine combustor and its turbomachinery.

A short description of the gas turbine simulator is given here; a more detailed description is given elsewhere (4-6). Figure 1 is a schematic of the 1-MM Btu/hr gas turbine combustor showing its internal design. Figure 2 is a photograph of the 1-MM Btu/hr gas turbine combustor. The head section of the turbine has an interchangeable, horizontal, flat-bladed air swirler for controlling the primary air-fuel spray and developing a recirculation zone in the rich combustion zone. A Delavan Swirl-Air nozzle with a 50° spray angle

Figure 1. Schematic of 1-MM Btu/hr gas turbine simulator.

Figure 2. Photograph of 1-MM Btu/hr gas turbine simulator.

is currently used as the atomizer. The pressurized combustion vessel itself is comprised of several short sections of refractory-lined stainless steel pipe. These sections are water-jacketed to provide cooling of the external pressure vessel wall. This modular design allows the length of the combustion zones to be varied. The removal of some of these modules allows the effect of residence time to be investigated under similar flow conditions.

The quench zone of the turbine simulator was designed to promote rapid mixing of the secondary air with the POC exiting the rich combustion zone, thus minimizing the occurrence of localized "hot spots" and the formation of thermal NO_x . A rotary control valve and a high-temperature-guided seat control valve are used to control the flow of combustion air entering the air preheater and the distribution of air between the rich and lean zones, respectively. The combustor is designed to operate at pressures up to 250 psig and a lean zone exit temperature of 2000°F.

A reduced flow area in the deposition section is used to increase the gas velocities up to those typically seen in the expander section of a gas turbine (400 to 800 ft/sec). Four air-cooled probes with various contact angles were machined from thick-walled high-temperature alloy tubing and were installed to simulate the leading edge of turbine blades. Additional cooling air was added after the first two probes to cool the exit gas stream up to 200°F, such that gas temperature as well as metal temperature can be investigated for their effects on deposition/erosion/corrosion (DEC). A spray water quench zone is located after the deposition section to spray high-pressure water into the combustion gases to cool the gases before passing them

through the rotary control valve used to back pressure the turbine simulator. A natural gas-fired fluidized-bed preheater is used to preheat the high-pressure combustion air to temperatures as high as 1000°F. Combustion efficiencies of the test fuels fired in the turbine simulator are calculated from gas and isokinetic particulate samples taken from both the rich and lean zones of the combustor.

3.2 High-Temperature, High-Pressure Cyclone

Figure 3 is a drawing showing the design of the high-temperature, high-pressure (HTHP) cyclone which has been inserted in the turbine simulator combustion system located at the EERC. This cyclone is fabricated from 8-inch schedule 40 pipe welded to form an off-center tee. This pipe is water-jacketed to keep the metal wall temperatures low. As shown in Figure 3, the cyclone dimensions are cast in refractory inside the tee. This cyclone replaced the last section of the lean combustion zone shown in Figure 1. Figure 4 shows the HTHP cyclone inserted in the gas turbine simulator combustion system. Openings have been included in the vessel walls for measuring the inlet and outlet combustion gas temperatures and pressures. In addition, openings have also been included for taking upstream particulate samples, while an existing port will allow downstream particulate samples to be collected for measuring the cyclone efficiency. A second opening was added for a water-jacketed and sealed baroscope viewing system which is currently being constructed. This baroscope will allow the flame quality and stability to be monitored during combustion tests.

3.3 Pressurized Drop-Tube Furnace

The emergence of advanced coal combustion technologies such as coal slurry-fired gas turbines requires fundamental knowledge of the fuel combustion processes at elevated pressures. Of critical importance is the basic combustion kinetics and the fate of coal mineral matter in such systems.

To address these issues, a pressurized drop-tube furnace was also constructed. The pressurized drop-tube furnace (PDTF) is capable of operating under the following conditions:

Temperature:	ambient to 2732°F (1500°C)
Pressure:	ambient to 300 psia (20.4 atm)
Oxygen:	0-20 mole%
Gas Flow:	0 to 7.8 scfm (220 L/min)
Residence Time:	0 to 5.0 sec

- Optical access at any residence time
- Provision for char and ash collection
- Provision for ash deposition studies

The design of the PDTF incorporates several novel features which allowed the design goals to be met. A drawing of the PDTF facility is given in Figure 5. The entire PDTF is constructed of standard 24" and 6" flanged pipe sections. The large pressure vessel contains the furnace sections of the PDTF as shown in Figure 6. Figure 7 is a photograph of the PDTF pressure vessel. The walls of the vessel are water-cooled to dissipate the heat from the furnaces. A preheater and two furnace sections are located above the

Figure 3. Design of HTHP cyclone for testing in 1-MM Btu/hr gas turbine simulator.

optical sight ports, and one furnace is located below the optical sight ports to reduce the temperature gradient across the optical access section. Optical access is provided by four 3" diameter ports in the pressure vessel. Electrical power is supplied to the furnaces by electrical feed through the terminals in the bottom blind flange of the pressure vessel.

Figure 4. Photography of HTHP cyclone in exit of lean combustion zone of 1-MM Btu/hr gas turbine simulator.

Above the large pressure vessel shown is the injector section containing the injector assembly. The injector is a 1-inch-diameter water-cooled probe sheathed in high-temperature insulation. Figure 8 is a photograph showing the translating mechanism used for raising and lowering the injector into the ceramic tube inside the furnace assembly. The injector may be retracted completely out of the furnace when not in use or may be lowered into the furnace to give the desired residence time between 0 and 5.0 seconds. Small viewports in the pipe crosses at the bottom and top of the injector section allow visual inspection of the probe and the sample-feeding behavior.

Below the large pressure vessel is a sampling probe assembly and translation mechanism. The sampling probe may be raised to the level of the optical access ports and retracted completely from the furnace for the removal of sample deposits or when not in use. Two pipe crosses with small sight ports allow inspection of the collection probe operation, and the removal of a blind flange provides access for the removal of sample deposits. The sampling probe tip is interchangeable to allow deposition or fly ash samples to be collected without removing the entire sample probe. Figure 9 shows the construction details of the sampling probe.

The sample feeder assembly is a blank flanged 6" pipe cross pressurized to slightly above the furnace pressure with gas connections to the furnace assembly. Figure 8 also shows the sample feeder pressure vessel located next to the sample injector translating mechanism. Figure 10 is a schematic of the coal feeder used in the PDTF. The design allows the actual sample feeder to be constructed of lightweight material, since it does not have to withstand

Figure 5. Pressurized drop-tube furnace process schematic.

more than slight pressure differentials. A small sight port allows inspection of the feeder operation, and the removal of a blind flange gives access to the vessel for filling or adjustment of the feeder. The lightweight feeder can then hang from a load cell in the pressure vessel to provide a continuous record of the sample feed rates. The gas composition and flow rate of gas

Figure 6. Furnace assembly in PDF vessel.

Figure 7. Photograph of PTFE pressure vessel.

Figure 8. Photograph of PDTF translating mechanism.

into the PDTF is controlled by oxygen and nitrogen mass flow controllers. Gas composition can be controlled between 0-20 mole % at flow rates up to 220 L/min. The furnace pressure is controlled by a letdown control valve at the exit of the furnace.

3.4 High-Pressure Atomization Spray Chamber

An existing pressure vessel has been modified to include observation ports to perform atomization studies under typical turbine operating pressures and air flows. The main objective of this work is to determine if differences in atomization quality account for the improvements in carbon burnout experienced with the LRC fuels. The design of the spray chamber involves an existing 11.25-inch-ID pressure vessel which has been modified to provide optical access perpendicular to the direction of the atomized spray. The optical access consists of two diametrically opposite 3" sight ports for the use of high-speed photography. In addition, a 2" sight port opposite of a 1" NPT port through which a sight pipe can be inserted has also been added. The use of a sight pipe reduces the length of the spray which the Malvern 2600's laser beam must pass through and eliminates the potential for vignetting which could occur if the beam were to pass through the complete spray cone. A honeycomb catalyst support is used as a flow straightener to provide a laminar flow of air around the atomizing nozzle. The height of the atomizer in relationship to the optical ports is adjustable from outside the pressure vessel, thus allowing the atomizer position to be changed during a single atomization test.

Figure 9. Schematic of PDTF sampling probe with interchangeable tips.

Figure 10. Schematic of coal feeder for pressurized drop tub furnace.

Figure 11 is a photograph of the pressurized spray chamber. The atomized slurry is collected in a funnel at the bottom of the spray chamber where it is drained off to a pressurized separation vessel. Pneumatic control valves are used to control the air flow rate and to back pressure the spray chamber. High-speed photography is accomplished using a high-speed strobe to backlight the slurry droplets during atomization. The use of high-speed photography allows droplet sizes larger than 564 microns (the top size for a Malvern particle-size analyzer with a 300-mm lens) to be detected and also provides information about the spray angle obtained under a given set of operating conditions.

An atomizer has been constructed which allows different types of atomizers to be utilized by simply changing the tip of the atomizer. Commercially available atomizers which can be utilized in the spray chamber are the internal-mixed Delavan Swirl-Air nozzles rated for 1.0 and 2.5 gallons-per-minute (gpm) liquid flow rates and a Delavan external mix atomizing air nozzle (Part #47283-1). The Swirl-Air atomizers are carbide-lined versions to reduce the amount of atomizer tip erosion experienced from the high-velocity CWF passing through the common orifice. The commercially available Parker Hannifan M2 (atmospheric combustion systems) and M6 (for pressurized combustion systems) can also be utilized. The EERC B-II nozzle made in-house for CWF testing in atmospheric combustion systems can also be utilized with large or small diameter orifice tips (0.175 and 0.125" ID).

3.5 Advanced Inorganic Analysis Techniques

Extensive research on the transformations of inorganic and mineral components in coal has been conducted at the EERC. Research has been performed to develop methods to determine the association, size, and composition of ash-forming constituents in coal. Techniques are now available to determine the distribution of phases in fly ashes, deposits, and slags. Fundamental studies of the transformation of inorganic components to form intermediate ash components in the form of vapors, liquids, and solids have been performed using advanced analytical techniques.

Current conventional analytical methods for coal and coal ash materials do not provide adequate detail regarding their complex chemical and mineralogical properties. Advanced analytical techniques are currently being used to determine the association and forms of inorganic components in coals (7,8) and coal ash-derived materials (9,10). In addition, other laboratory-scale techniques are routinely used to determine viscosity, surface tension, sintering behavior, and deposit strength development (11,12). Utilization of these advanced analytical techniques, coupled with other laboratory methods, can potentially provide significant advances in understanding the behavior of inorganic components during combustion that will ultimately lead to better methods to predict and mitigate ash-related problems.

3.5.1 SEM Techniques

Automated scanning electron microscope/microprobe (SEM/EMPA) techniques are an effective means to examine coals, fly ashes, deposits, slags, soils, cements, and other complex heterogeneous materials. For example, these techniques provide the information needed to elucidate mechanisms of inorganic transformations which form intermediate ash, deposits, and slags during combustion and gasification. The SEM/EMPA system allows for observation and

Figure 11. Photograph of pressurized spray chamber.

chemical analysis of very fine-grained phases while simultaneously preserving both the original chemistry of the minerals and their relationships to the organic constituents. Widespread applications of SEM/EMPA to coal include localized observation of the elemental content of macerals, determination of the morphology of organic maceral structures, identification of minerals, and description of the morphology of minerals. Automated SEM/EMPA and automated image analysis (AIA) techniques have been developed to quantify coal minerals. The automated SEM/EMPA techniques rely on the characterization of statistically significant numbers of particles to produce quantitative data on their size and chemistry.

Three SEM/EMPA techniques, computer-controlled scanning electron microscopy (CCSEM), scanning electron microscopy point count (SEMP), and automated image analysis (AIA), are presently used in ash behavior in combustion and gasification systems research at the EERC. These techniques permit the study of transformations of inorganic constituents from the initial stages of coal conversion through the transformations that occur during ash deposition and slag formation. Their specific applications include 1) determination of the size, composition, and association of minerals in coals, 2) determination of the size and composition of intermediate ash components and fly ash, 3) determination of the degree of interaction (sintering) in ash deposits, and 4) identification and quantification of the components of ash deposits and slags--this includes liquid phase composition, reactivity, and crystallinity. By using SEM/EMPA for coals and throughout all stages of utilization, a continuity of data is achieved. The techniques which are routinely used by the Inorganic Analysis Research Lab (IARL) for examination of the inorganic components in coal and coal-derived materials are briefly described below.

CCSEM (7) is used to characterize unaltered coal samples and inorganic combustion products. A computer program is used to locate, size, and analyze particles. Because the analysis is automated, a large number of particles can be analyzed quickly and consistently. The heart of the CCSEM analysis system is a recently installed annular backscattered electron detector (BES). The BES system is used because the coefficient of backscatter (the fraction of the incoming beam that is backscattered) is proportional to the square root of the atomic number of the scattering atoms. This permits a high degree of resolution between sample components based on their atomic numbers. This means that coal minerals can be easily discerned from the coal matrix, and fly ash particles can be easily discerned from epoxy in polished sections. Brightness and contrast controls are used to optimize threshold levels between the coal matrix and mineral grains or fly ash particles. When a video signal falls between these threshold values, a particle is discerned and the particle center located. A set of eight rotated diameters about the center of the particle are measured, and the particle area, perimeter, and shape are calculated. The beam is then repositioned to the center of the particle, and an x-ray spectrum is obtained. The information is then stored to a Lotus transportable file for data reduction and manipulation. The CCSEM data provides quantitative information concerning not only the mineral types which are present, but their size and shape characteristics as well. Since the same analysis can be performed on the initial coal and resultant fly ash, direct comparisons can be made and inorganic transformations inferred.

The primary method used to characterize deposits is the scanning electron microscope/microprobe. The SEM is capable of imaging deposits and

determining the chemical composition of areas within deposits down to 1 micrometer in size. The use of the SEM is extremely valuable in identifying materials responsible for deposit initiation, growth, and strength development as well as the characterization of significant slag properties such as reactivity and viscosity. The SEM technique most often used to characterize entrained ashes and deposits is the SEMPC (8,9). This technique was developed to quantitatively determine the relative amount of phases present in ashes and deposits. The method involves microprobe analysis (chemical compositions) of a large number of random points in a polished cross section of a sample. In addition, x-ray diffraction is used to determine the crystalline phases present in the deposit as a support for the SEMPC analysis. Bulk chemical analysis of the deposit is also performed with x-ray fluorescence. This technique provides information on the degree of melting and interaction of the various deposited ash particles and provides quantitative information on the abundance of phases present in the ash. By examining the phases present, the material responsible for the formation of the deposit can be identified. In addition, various regions in deposits and individual entrained ash particles can be examined to determine the changes that occurred with time and, possibly, with changes in coal composition.

The CCSEM and SEMPC techniques are supplemented with morphological and chemical analysis of the microstructural features of the deposit. This is performed either by manually scanning across the sample, elemental mapping, or AIA. Automated digital imaging allows for the rapid, objective collection of digital images. Once the digital images have been collected and saved to disk, they can be manipulated in many constructive ways. Numerous applications for the digital images have been implemented at the EERC. Two methods using AIA to enhance the utility of the CCSEM and SEMPC techniques are described below.

The CCSEM technique described above is used for the standard analysis of coal. However, more detailed analysis of the coal minerals may be necessary. During pulverization of the coal, some coal minerals are liberated from the coal matrix. The mineral grains liberated from the matrix will experience different conditions and undergo different transformations and reactions than the minerals present within the coal matrix. Therefore, whether a mineral is contained within the coal matrix (included) or is separated from the coal matrix (excluded) is important when considering coal combustion. The term juxtaposition refers to mineral-to-mineral relationships and the relationship of minerals to the organic matrix of the coal.

The present method (7) used to determine the included/excluded and juxtaposition of the coal mineral matter involves the standard CCSEM analysis of the coal. However, prior to the analysis of each frame examined, a digital backscattered image is obtained and saved to the TN8500 image analysis system. As the CCSEM analysis proceeds each particle analyzed is identified on the image. The data can then be modified to include juxtapositional relationships.

The SEMPC technique does not provide all of the information needed to fully characterize a deposit or other material. It is also important to examine the morphology and physical relationships of the microscopic components of the deposit. While the SEMPC technique quantifies the chemistry and phase distributions, the morphologic characterization of deposits reveals the size, crystallinity, and juxtaposition of the phases present. The

morphologic investigation of the deposits provides insight into the sintering process as evidenced by the growth of necks between particles and the formation of a captive surface.

The major problem with morphologic information from the SEM is that it tends to be subjective, with the operator choosing areas of interest. A new technique (10) under development at the EERC will combine the SEMPC analysis with the morphologic investigation. The new analysis will collect quantitative chemical data from a grid pattern just as the present SEMPC program does; however, the new analysis will automatically collect digital images and save them to disk. The location of the points where EDS were collected will be plotted on the digital images. This will allow for detailed investigations of the positions of the phases identified by SEMPC. When combined with automated digital image analysis, this program will produce data detailing the chemistry, morphology, and juxtapositional nature of coal minerals and ash. These data will permit the quantification of parameters such as neck growth in deposits or thickness and composition of glassy phases in deposits and fly ash grains. The technique is currently being used to assess the characteristics of deposits produced in laboratory-, pilot-, and full-scale coal combustion systems. The SEMPC technique is combined with other methods of analysis to identify the compounds in the deposit that are causing the deposition problem. This information is used to trace the origin of the liquid phases back to the minerals and organically associated inorganic constituents in the original coal.

3.5.2 Sintering Behavior

Sintering is the process of consolidation of a solid substance of high surface area (for example, a powder) to a solid mass. In this process, the density of a given mass of sample will decrease compared to the initial sample. The sintering process is very important, because it is responsible, at least in part, for the formation of agglomerates, clinkers, and slags in coal combustion systems.

The sintering process requires mass transfer to occur. In the case of ash systems, the predominant mass transfer process is via viscous flow of liquid phase between adjacent particles. The relation of viscosity and surface tension to the sintering process has been discussed above. However, it is necessary to establish the rate at which the sintering occurs and the effect of viscosity and surface tension on the rate of sintering.

In sintering experiments, ash from a coal is produced under appropriate conditions to simulate various utilization environments. The density of the sintered masses will be determined using a pycnometer. Furthermore, the samples will be analyzed using x-ray diffraction, scanning electron microscopy, electron microprobe, and SEMPC. The detailed analysis will establish the various phases present and their relation to the sintering process. In particular, the SEMPC analysis will be used to establish the chemical composition of the component liquid phases responsible for sintering. The chemical composition will be used to predict the viscosity and surface tension of the component liquid phases.

3.5.3 XRF/XRD

The elemental content of bulk coal combustion products is determined by energy dispersive x-ray fluorescence spectrometry. Homogeneous finely ground sample powders are pressed into pellets and analyzed in a vacuum using a Kevex x-ray spectrometer equipped with a rhodium x-ray tube and six secondary targets. Interelement matrix effects are corrected for by using the EXACT (energy dispersive x-ray analysis computation technique) fundamental parameter routine. Calibration constants are derived from the analysis of certified standard reference materials and synthetic standards prepared from certified compounds. Analytical precision and accuracy are evaluated and optimized by analyzing at least one well-characterized coal ash standard during each analysis run. A new Kevex XRF system has been installed and will be in operation soon. The new system will increase our bulk chemical analysis abilities.

Qualitative x-ray powder diffraction is used to identify the crystalline phases present in coal combustion products. A representative aliquot of each sample powder is ground with ethyl alcohol and smeared onto a single-crystal, "zero"-background, quartz plate for subsequent analysis. Diffraction data are collected in 0.02° steps for a 1-second dwell time using a Phillips automated diffractometer equipped with a copper tube, theta-compensating slit, graphite-diffracted-beam monochromator, and scintillation detector. Software programs supplied by Materials Data Incorporated are used for data collection, data reduction, and phase identification.

3.5.4 The Chemical Fractionation Technique

The chemical fractionation procedure (11) is used to determine the modes of occurrence of inorganics present in coals. Chemical fractionation is especially valuable when the inorganics present in low-rank coals, which contain significant quantities of inorganics present as the salts of organic acid groups in the coal, are examined. CCSEM can determine the quantity of discrete minerals present in coals so, when combined with chemical fractionation, all of the inorganics present in coals can be determined.

The chemical fractionation procedure involves successive extractions with H_2O , 1 molar NH_4OAc , and 1 molar HCl . The elements that are extracted by H_2O are present in the coal as water-soluble compounds. Those that are extracted by NH_4OAc are present in an ion-exchangeable association (principally as the salts of carboxylic acids) that can be ion-exchanged for an ammonium ion from the solution, although gypsum ($CaSO_4 \cdot 2H_2O$) also dissolves during this extraction. HCl -extractable elements are present in the coal as acid-soluble minerals such as carbonates or sulfates, or in organic complexes with high coordination numbers.

3.5.5 Surface Science

Scanning Auger microscopy (SAM) is used for comprehensive surface analysis of a wide range of coal and coal-related materials. Capable of determining surface composition, chemical states, and depth profiling, the PHI 595 multiprobe instrument consists of three analytical systems: an Auger electron spectroscopy (AES) system capable of a 50×10^{-9} -meter-diameter electron beam, a cylindrical mirror electron analyzer, and a scanning system

and secondary electron detector to permit surface elemental mapping and high-resolution photographs. A 5-kV differentially pumped argon ion beam gun provides sputter-etching capability to acquire depth profile information. The x-ray photoelectron spectroscopy (XPS) system has a 10-kV Mg x-ray source and a beam diameter of about 2 mm. A double-pass, cylindrical mirror electron analyzer provides surface composition and chemical states. A secondary ion mass spectroscopy (SIMS) system utilizes the ion gun to ablate the sample surface to obtain trace element, isotopic, and molecular information. The positive and negative ions produced from the surface are analyzed by an energy-filtered quadrupole mass spectrometer.

3.6 Determination of Deposit Strengths

Deposits formed in the drop-tube furnace are removed from the coupon and measured for strength. The apparatus used to determine the crushing strength of ash deposits formed in the drop-tube furnace is shown in Figure 12. It consists of a miniature horizontal translator and a miniature pressure transducer. The translator (Ealing Electro Optics Model 37-0254) has a range of travel of 25 mm, a resolution of 0.1 μm , and a maximum translational speed of 15 mm/min. The pressure transducer (Precision Measurement Company Model 156) is a diaphragm strain gauge design with one active sensing face. The pressure range is 0-1000 psi. The transducer output is attached to a strain transducer indicator (Precision Measurement Company Model X). The transducer is mounted in a slot on top of an aluminum block and attached to the horizontal translator. A rod inserted in the side of the block meets the sensing face of the transducer and transmits the force exerted on the deposit as the translator moves.

4.0 RESULTS AND ACCOMPLISHMENTS

4.1 Fuel Preparation and Analyses

In order to learn about the potential for ash deposition on turbine blades, advanced analytical techniques were used to characterize raw Spring Creek coal and its beneficiated product to determine the abundance, size, and association of the inorganic constituents. The primary methods of analysis, in addition to conventional ASTM ashing followed by determination of the ash components, include chemical fractionation and computer-controlled scanning electron microscopy (CCSEM), used to determine the abundance of inorganic components associated both organically and inorganically in the coal. Chemical fractionation provides a means to determine the abundance of inorganic elements associated with the organic structure of the coal, while CCSEM is used to determine the size and composition of discrete mineral grains within the coal.

Tables 1 and 2 show the proximate, ultimate, and ash analyses of the three coals tested in the PDTF. The coals consisted of a raw Spring Creek coal; a Spring Creek coal which had been physically cleaned in a heavy media separator, acid-cleaned in a weak nitric acid leaching column and hot-water dried (HWD) and micronized; and a Spring Creek coal which had only been HWD and micronized (this fuel was supplied to Allison Gas Turbine Division for testing in their proof-of-concept coal-fired gas turbine). It can be seen from these analyses that the more deeply cleaned the coal, the lower the ash and sodium levels in the ash.

Figure 12. Deposit-strength measuring apparatus.

Chemical fractionation results for the Spring Creek coal are listed in Tables 3 and 4. These tables show the chemical fractionation results for the raw coal and the hydrothermally treated coal. Chemical fractionation was not performed on the acid-cleaned coal since little change in the amount of soluble cations was expected. For the raw coal, the solubility of the elements is very low, with the exception of phosphorus, calcium, sodium, potassium, and magnesium; this indicates that these elements are present primarily as the salts of organic acid groups, or as soluble minerals such as carbonates. The calcium was leached out with both ammonium acetate and HCl. The calcium removed by HCl may have been present as acid-soluble carbonate material, although CCSEM analysis indicates otherwise. The amount removed by ammonium acetate may reflect the presence of gypsum and organically bound calcium. A significant portion of the iron (16%) was also removed with ammonium acetate, indicating that some of the iron may be present in an ionic form. The remainder of the inorganic elements are present as discrete mineral grains, as indicated by their relative insolubility. The major differences between the raw coal and the CWF chemical fractionation results are consistent with the changes one would expect in inorganic content resulting from the treatment process. It appears that most of the salts of organic acid groups and soluble minerals are removed by the HWD process.

Tables 5 through 7 show the results of the CCSEM analysis on the PC/AC/HWD/micronized, the HWD/micronized, and the raw coals. The CCSEM analysis of the PC/AC/HWD/micronized Spring Creek fuel indicates that the fuel is concentrated in quartz, aluminosilicates, pyrite, and iron oxide, although

TABLE 1

Proximate and Ultimate Analyses of Fuels Tested

Sample:	Raw Spring Creek Coal	HWD Spring Creek	PC/AC/HWD Spring Creek
PDU Test No.	NA	55	45
Prox. Anal. (mf)			
Volatile Matter	43.48	42.82	39.62
Fixed Carbon	51.70	52.58	56.21
Ash	4.82	4.60	2.07
Ult. Anal. (mf)			
Hydrogen	4.75	4.66	4.51
Carbon	72.52	73.22	75.00
Nitrogen	0.86	0.97	1.37
Sulfur	0.41	0.40	0.35
Oxygen (diff.)	16.94	16.12	16.70
Ash	4.82	4.60	2.07
Heating Value (mf, Btu/lb)	12,260	12,693	12,820
Ash Fusion Temp. Deg F-Reducing			
Init. Deform.	ND	ND	2,148
Softening	ND	ND	2,278
Hemispherical	ND	ND	2,310
Fluid	ND	ND	2,313
Part. Size-Mean (microns)	54	13	15
Top Size (99%<) (microns)	348	100	81

TABLE 2

X-Ray Fluorescence Analysis of LRC Fuels Tested in Turbine Program:
High-Temperature Ash Results (% of ash, SO₃-free)

Sample:	Raw Spring Creek Coal	HWD Spring Creek	PC/AC/HWD Spring Creek
PDU Test No.	NA	55	45
SiO ₂	29.2	31.0	33.5
Al ₂ O ₃	18.7	21.3	31.9
Fe ₂ O ₃	8.1	9.6	14.7
TiO ₂	2.3	2.0	3.3
P ₂ O ₅	1.2	0.6	0.9
CaO	23.0	22.0	10.1
MgO	7.6	7.8	4.3
Na ₂ O	9.0	5.5	1.0
K ₂ O	0.8	0.2	0.2
Total	99.9	100.0	99.9

TABLE 3

Chemical Fractionation Results of Raw Spring Creek Coal (wt%)

	Initial (ppm)	Removed by H ₂ O	Removed by NH ₄ OAc	Removed by HCl	Remaining
Silicon	4273	0	0	0	100
Aluminum	3997	3	6	49	42
Iron	2442	0	16	72	12
Titanium	604	0	45	0	55
Phosphorus	315	2	73	22	3
Calcium	6688	0	59	40	0
Magnesium	2024	1	79	17	2
Sodium	3058	34	65	1	1
Potassium	790	65	25	2	8

* Results are expressed with silicon loss normalized to zero.

TABLE 4

Chemical Fractionation Results of Hydrothermally Treated
Spring Creek Coal (wt%)

	Initial (ppm)	Removed by H ₂ O	Removed by NH ₄ OAc	Removed by HCl	Remaining
Silicon	7702	0	0	0	100
Aluminum	4634	0	0	0	100
Iron	2712	6	4	45	44
Titanium	427	0	3	0	97
Phosphorus	108	0	12	64	24
Calcium	6902	0	30	55	15
Magnesium	2725	0	42	51	7
Sodium	489	6	82	3	9
Potassium	161	0	20	0	80

* Results are expressed with silicon loss normalized to zero.

the high iron oxide levels could also be due to contamination from the magnetite heavy media used in the physical cleaning process. CCSEM analysis of the Allison fuel and the raw coal shows that the dominant minerals present are quartz and kaolinite, with significant amounts of other aluminosilicates, including montmorillonite, and potassium aluminosilicate. The presence of a significant amount of pyrite was also noted. The results indicate that the hot-water-drying process slightly reduced the total amounts of inorganic constituents present; however, the relative amounts of discrete minerals remained constant. The CCSEM size analysis indicates that the micronized coals were dominated by minerals in the 2.2- to 10.0-micrometer size range while the size distribution of minerals in the raw coal was much more

TABLE 5

Summary of CCSEM Results for PC/AC/HWD Spring Creek Fuel

Particle-Size Distribution, μm : Wt% Mineral Basis	<2.2	2.2- 4.6	4.6- 10.0	10.0- 22.0	22.0- 46.0	>46.0	Total
Quartz	15.7	14.9	0.6	0.0	0.0	0.0	31.1
Iron Oxide	3.6	5.5	0.0	0.0	0.0	0.0	9.1
Aluminosilicate	26.9	11.5	1.1	0.0	0.0	0.0	39.5
Ca Al-Silicate	0.0	0.2	0.0	0.0	0.0	0.0	0.2
Fe Al-Silicate	0.2	0.0	0.0	0.0	0.0	0.0	0.2
K Al-Silicate	1.0	0.2	0.0	0.0	0.0	0.0	1.2
Pyrite	7.7	1.4	0.0	0.0	0.0	0.0	9.1
Barite	0.0	0.2	0.0	0.0	0.0	0.0	0.2
Gyp/Al-Silicate	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Ca Aluminate	0.2	0.1	0.0	0.0	0.0	0.0	0.3
Spinel	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Rutile	0.4	1.1	0.0	0.0	0.0	0.0	1.5
Pyrrhotite/Sulfate	0.4	0.0	0.0	0.0	0.0	0.0	0.4
Si-rich	0.5	2.4	0.0	0.0	0.0	0.0	2.9
Unknown	1.7	2.0	0.6	0.0	0.0	0.0	4.3
Total	58.3	39.5	2.2	0.0	0.0	0.0	100.0

dispersed. Obviously, the processing preferentially removes some of the larger minerals and reduces the size of the remaining minerals. This is an important factor when considering ash behavior because it affects both ash particle chemistry and aerodynamic behavior in the utilization system.

Tables 8 and 9 show the CCSEM analysis with image analysis for determining juxtaposition of the mineral particles for both the Allison HWD/micronized and raw Spring Creek fuels. These tables indicate that the cleaned coals tend to contain more inherent coal particles presumably because the physical cleaning and centrifugation processes would separate the finer mineral particles.

4.2 Coal-Water Fuel Atomization

Due to manpower and equipment constraints, very limited CWF atomization testing was completed during the reporting period.

Spray testing of Spring Creek CWF was conducted during the reporting period using a new Delavan external mix atomizer. These atomization tests were conducted to obtain high speed photographs using this new atomizer. Results from these atomization tests indicate that the atomizer had a lower pressure ratio at comparable atomizing air-to-fuel ratios than the Delavan external mix atomizer. These photographs indicated that at the lower atomizing air-to-fuel ratios (< 1.25) the spray pattern was becoming much less dispersed. It was apparent that this atomizer was significantly oversized for the flowrates utilized in these tests and did not provide very meaningful information.

TABLE 6

Summary of CCSEM Results for HWD/Micronized Spring Creek Fuel
Produced for Allison Gas Turbines

Particle-Size Distribution, μm : Wt% Mineral Basis	<2.2	2.2- 4.6	4.6- 10.0	10.0- 22.0	22.0- 46.0	>46.0	Total
Quartz	15.0	7.9	1.3	0.8	0.5	0.0	25.5
Iron Oxide	2.1	2.2	0.0	0.0	0.0	0.0	4.4
Rutile	0.9	0.7	0.0	0.0	0.0	0.0	1.7
Alumina	0.3	0.0	0.0	0.0	0.0	0.0	0.3
Calcite	0.3	0.3	0.0	0.0	0.0	0.0	0.6
Dolomite	0.0	0.0	0.7	0.0	0.0	0.0	0.7
Kaolinite	11.2	8.2	2.8	0.2	0.0	0.0	22.4
Montmorillonite	5.5	2.2	0.0	0.0	0.0	0.0	7.7
K Al-Silicate	1.0	0.6	0.0	0.0	0.0	0.0	1.6
Fe Al-Silicate	0.3	0.2	0.0	0.0	0.0	0.0	0.5
Ca Al-Silicate	1.1	0.7	0.0	0.1	0.0	0.0	1.7
Aluminosilicate	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Mixed Al-Silicate	0.6	0.0	0.0	0.0	0.0	0.0	0.6
Fe Silicate	0.0	0.8	0.0	0.0	0.0	0.0	0.8
Ca Silicate	0.1	0.2	0.0	0.0	0.0	0.0	0.4
Pyrite	4.7	0.6	0.0	0.0	0.0	0.0	5.3
Pyrrhotite	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Oxidized Pyrrhotite	0.9	0.9	0.0	0.3	0.0	0.0	2.0
Gypsum	0.2	0.0	0.0	0.0	0.0	0.0	0.2
Barite	1.8	1.1	0.0	0.0	0.0	0.0	3.0
Apatite	0.0	0.2	0.0	0.0	0.0	0.0	0.2
Ca Al-P	0.5	1.2	0.0	0.0	0.0	0.0	1.7
Gypsum/Barite	0.8	0.0	0.0	0.0	0.0	0.0	0.8
Gyp/Al-Silicate	0.5	0.2	0.0	0.3	0.0	0.0	0.9
Si-Rich	0.5	0.8	0.0	0.4	0.7	0.0	2.3
Ca-Rich	0.2	0.0	0.0	0.0	0.0	0.0	0.2
Ca-Si Rich	0.1	0.0	0.0	0.0	0.0	4.5	4.6
Unknown	5.4	0.6	0.9	1.8	1.1	0.0	9.8
Total	54.0	29.8	5.6	3.8	2.3	4.5	100.0

Atomization tests utilizing a Spring Creek CWF and the Delavan Swirl-Air nozzle employed in previous combustion testing were also attempted during the reporting period. Observation of the spray cone indicated that at the lower atomizing air-to-fuel ratios the spray would become flat. The atomizing air-to-fuel ratio at which the spray would become flat increased with increasing spray chamber pressure. The reason for this nozzle behavior is not understood at this time, but it is felt that this phenomenon did not occur during the combustion tests performed in 1-MM Btu/hr gas turbine simulator using this same atomizer.

4.3 PDTF Combustion Testing With Beneficiated Fuels

Pressurized drop-tube furnace (PDTF) testing was conducted using the fuels described above. A series of shakedown tests was conducted to measure

TABLE 7

Summary of CCSEM Results for Raw Spring Creek Fuel (-325 mesh)

Particle-Size Distribution, μm : Wt% Mineral Basis	<2.2	2.2- 4.6	4.6- 10.0	10.0- 22.0	22.0- 46.0	>46.0	Total
Quartz	4.0	5.3	4.5	4.6	4.1	0.0	22.4
Iron Oxide	0.2	0.1	1.0	0.7	0.4	2.5	4.9
Rutile	0.2	0.0	0.3	0.1	0.0	0.0	0.7
Calcite	0.3	0.3	0.0	0.0	0.0	0.0	0.6
Kaolinite	1.9	2.8	4.7	4.9	5.6	2.4	22.3
Montmorillonite	0.5	1.1	0.9	0.5	1.2	0.0	4.1
K Al-Silicate	1.0	2.0	1.8	1.0	1.1	0.0	6.9
Fe Al-Silicate	0.2	0.0	0.0	0.1	0.0	0.0	0.2
Ca Al-Silicate	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Aluminosilicate	0.2	0.6	1.1	0.1	0.0	0.0	2.0
Mixed Al-Silicate	0.1	0.2	0.0	0.0	0.2	0.0	0.4
Pyrite	1.1	0.4	0.9	1.1	2.5	1.1	7.2
Pyrrhotite	0.2	0.0	0.0	0.1	0.6	0.0	0.8
Oxidized Pyrrhotite	0.0	0.3	0.0	0.0	0.0	0.0	0.4
Gypsum	0.3	1.2	0.0	0.1	0.2	0.0	1.8
Barite	0.7	0.5	0.9	0.3	0.7	0.0	3.1
Ca Al-P	0.1	0.4	0.0	0.2	0.0	0.0	0.7
Gypsum/Barite	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Gyp/Al-Silicate	0.2	0.0	0.0	0.4	0.0	1.0	1.6
Si-Rich	0.5	0.9	1.0	0.8	1.6	2.4	7.1
Ca-Rich	0.1	0.2	0.0	0.0	0.0	0.0	0.3
Unknown	1.6	1.4	0.9	3.3	4.8	0.0	12.0
Total	13.7	17.6	18.0	18.4	22.8	9.4	100.0

the carbon burnout achieved using the Allison fuel (HWD/micronized) Spring Creek (AFSPC). After optimization of the burnout tests, other fly ash collection tests were conducted using the physically cleaned, acid-cleaned, HWD/micronized Spring Creek (APSPC) and the raw Spring Creek (SPCRK) fuels. Tables 10 through 14 show the operating conditions, weights of fly ash collected, and the measured burnouts for these combustion tests. Percent ash in the fly ash was measured using a modified TGA technique since sample sizes were too small to perform ASTM loss-on-ignition (LOI) tests. Carbon burnout was calculated using the equation given below by Wenglarz and others (13):

$$\text{Carbon burnout fraction} = (1 - W_a/W_x)/(1 - W_a)$$

where W_x is the weight fraction of ash in the particulate sample and W_a is the weight fraction of ash in the coal from which the slurry was made.

Initial combustion tests were performed using a bulk filter to capture all of the fly ash. Starting with Test Number 37, the number 2 and 5 cyclones of a multicyclone set along with a final filter were used to collect size-fractionated fly ash samples. The three fractions were then submitted for analysis by SEM point count, particle size using the small sample cell on a Malvern 2600, and LOI tests using the modified TGA technique if enough sample

TABLE 8

CCSEM Analysis with Image Analysis for Allison HWD/Micronized
Spring Creek Fuel

Mineral Types	Number	Frequency	% Extraneous	% Inherent
Quartz	22	20.56	23	77
Montmorillonite	5	4.67	20	80
K-Aluminosilicate	2	1.87	0	100
Kaolinite	15	14.02	27	73
Ca-Aluminosilicate	1	0.93	0	100
Ca-Silicate	1	0.93	0	100
Oxidized Pyrrhotite	2	1.87	50	50
Pyrite	6	5.61	17	83
Gypsum	1	0.93	0	100
Mixed Silicates	1	0.93	0	100
Gypsum/Aluminosilicate	3	2.80	33	67
Si-Rich	5	4.67	40	60
Ca-Si-Rich	1	0.93	0	100
Fe-Al-Silicate	1	0.93	0	100
Unknown	41	38.32	7	93
Total	107	100.0		

remained. Entrained alkali gettering tests (SPCRK 42 and 43) were performed by adding kaolin to the raw Spring Creek at a level that would increase the ash content by approximately 50 percent.

Tables 15 through 20 show the scanning electron microprobe point count (SEMPC) and particle-size analyses of the fly ash samples from samples analyzed to this point. Other analyses will be performed at a later date as analytical time on the SEM becomes available. Analyses of the raw Spring Creek fly ash indicate that the final filter is high in sodium sulfates and sodium calcium sulfates, which would be expected to cause severe alkali deposition and corrosion problems in a coal-fired gas turbine. Addition of the kaolin to the raw Spring Creek appeared to affect the distribution of the sodium species reducing the amount of sodium species found in the smallest size range (i.e., final filter). Figures 13 and 14 show the weight percent of the total elements as collected in each size fraction. As can be seen the addition of the kaolin reduced the percent of Na_2O collected in the final filter by a factor of two. Operating pressure did not seem to affect this shift in where the sodium species are collected. The cut points of the multicyclones were significantly different under atmospheric pressure such that a direct comparison cannot be made.

A comparison of the fly ash composition and particle-size distribution is also given in these tables. Both the PC/AC/HWD/micronized and the Allison HWD/micronized Spring Creek fuels had lower sodium levels in the final filter fraction than the raw Spring Creek fuel. This is expected since acid-cleaning and hot-water-drying processes have been shown to reduce the sodium levels of the coal ash. However, it also appears that the HWD/micronized Spring Creek fuel has lower sodium levels than the more deeply cleaned Spring Creek fuel, which is not expected. One possible explanation is that the CCSEM analyses

Figure 13. Weight percent of total elements in each size fraction for Spring Creek coal combustion testing at 100 psi with and without Kaolin addition.

Figure 14. Weight percent of total elements in each size fraction for Spring Creek Coal combustion testing at atmospheric pressure with and without kaolin addition.

TABLE 9

CCSEM Analysis with Image Analysis for Raw Spring Creek Fuel				
Mineral Types	Number	Frequency	% Extraneous	% Inherent
Quartz	102	24.46	39	61
Montmorillonite	10	2.40	60	40
K-Aluminosilicate	23	5.52	61	39
Kaolinite	90	21.58	58	42
Iron Oxide	5	1.20	60	40
Ca-Aluminosilicate	2	0.48	50	50
Na-Aluminosilicate	1	0.24	0	100
Rutile	3	0.72	0	100
Pyrrhotite	3	0.72	33	67
Oxidized Pyrrhotite	1	0.24	100	0
Pyrite	13	3.12	54	46
Gypsum	9	2.16	67	33
Barite	12	2.88	58	42
Calcite	5	1.20	80	20
Ca-Al-Phosphate	3	0.72	33	67
Mixed Silicates	1	0.24	0	100
Aluminosilicate	3	0.72	33	67
Gypsum/Barite	1	0.24	0	100
Gypsum/Aluminosilicate	7	1.68	29	71
Si-Rich	22	5.28	59	41
Ca-Rich	4	0.96	0	100
Fe-Al-Silicate	2	0.48	50	50
Unknown	95	22.78	26	74
Total	417	100.00		

indicate that a significant quantity of kaolinite appears in the small size ranges of the Allison fuel, while there appears to be no kaolinite in the deeply cleaned fuel. The deep cleaning appears to remove some inorganic components which might be acting as effective alkali getters, thus accounting for the sodium concentration increase in the more deeply cleaned fuel.

Particle-size analyses of these fractions as determined by the small sample cell on the Malvern 2600 indicate that the final filter tended to have the largest particle-size distribution among the three collection devices (i.e., the #2 and #5 cyclones and the final filter) which is physically impossible given the operating principles of a multicyclone sampling system. Further examination of the final filter samples was conducted by SEM. Figures 15 and 16 are high-magnification photographs of filter cake from a final filter sample. These photographs indicate that the filter cake consists of very fine ($< 1 \mu\text{m}$) particles which have agglomerated into larger flakes. It is believed that the Malvern particle-size distribution actually is measuring the size of the agglomerated flakes.

The PDTF testing has also been directed to perform tests for a separate multiclient contract concerning coal ash behavior under reducing environments. No PDTF testing under this project was completed during the last two months of the reporting period.

Figure 15. Photograph of flakes of final filter cake.

Figure 16. High-magnification photograph of final filter cake.

TABLE 10

Operating Conditions and Results from Shakedown Combustion Tests Using Allison Fuel Spring Creek Coal

	AFSPC01	AFSPC02	AFSPC03	AFSPC04	AFSPC05	AFSPC07	AFSPC08	AFSPC09	AFSPC10	AFSPC11	AFSPC14
Coal Feed Rate (g/min)	0.1530	0.1209	0.0679	0.3376	0.1405	0.3955	0.1134	0.4213	0.2454	0.4485	0.3913
Total Weight Coal Fed (g)	2.3	4.3	1.7	6.6	6.2	11.7	3.7	9.5	6.4	9.0	10.2
Weight Ash Collected (g)	0.0917	0.6923	0.2000	0.3247	0.1726	0.4123	0.1837	0.2869	0.2602	0.2188	.1545
Weight Ash Feed (g)	0.1058	0.1978	0.0782	0.3036	0.2852	0.5382	0.1702	0.4370	0.2944	0.4140	0.4504
Percent Ash in Fly Ash (mf)	47.4	5.44	10.97	12.86	13.05	19.64	8.19	12.73	15.33	26.41	69.88
Fly Ash Carbon Burnout (%)	94.65	16.19	60.87	67.33	67.87	80.27	45.95	66.94	73.37	86.56	97.92
Feeder Air Flow Rate (slpm)	20.0	20.0	8.0	10.0	11.2	10.0	10.0	10.0	10.0	10.0	8.0
Avg. Air Flow Rate (slpm)	99.9	99.9	15.0	39.9	39.9	39.9	39.9	39.9	89.9	39.7	5.0
Avg. N ₂ Flow Rate (slpm)	99.9	99.9	15.0	50.0	50.0	49.9	49.9	49.9	89.7	49.9	13.0
Initial Oxygen Conc. (mol%)	11.5	11.5	12.7	10.5	10.6	10.5	10.5	10.5	11.0	10.5	10.5
% Excess Air	10,746	13,624	4,592	1,945	4,937	1,646	5,988	1,540	5,535	1,433	195
Exit Gas Equivalence Ratio	0.0092	0.0073	0.0213	0.0489	0.0199	0.0573	0.0164	0.0610	0.0177	0.0652	0.3393
PDTF Pressure (psig)	133.3	133.3	3.1	5.6	5.4	5.4	5.1	4.9	19.2	7.2	1.1
Zone 1 Tube Temp. (°C)	1,197	1,128	1,248	1,198	1,398	1,398	1,398	1,398	1,251	1,395	1,267
Zone 2 Tube Temp. (°C)	1,248	1,247	1,248	1,198	1,398	1,398	1,398	1,398	1,370	1,398	1,298
Zone 3 Tube Temp. (°C)	1,245	1,245	1,245	1,195	1,218	1,229	1,396	1,229	1,226	1,225	1,296
Optical Zone Temp. (°C)	798	773	952	872	907	899	972	792	882	910	1,055
Zone 4 Tube Temp. (°C)	815	800	1,247	1,197	1,197	1,197	1,342	998	1197	1197	1,283
Substrate Metal Temp. (°C)	199	188	67	148	154	169	188	169	160	176	40
Prim. Gas Vel. (m/s)	2.03	2.03	6.75	7.37	8.39	7.48	7.56	7.69	4.45	6.91	7.71
Total Gas Vel. (m/s)	0.41	0.41	0.59	1.32	1.37	1.36	1.54	1.40	1.53	1.25	0.47
Accelerator Gas Vel. (m/s)	14.8	59.3	21.4	47.5	49.4	49.1	55.4	50.3	55.2	45.0	17.0
Avg. Residence Time (s)	0.97	0.97	0.93	0.47	0.45	0.46	0.40	0.45	0.41	0.50	0.85

TABLE 11

Operating Conditions and Results from Shakedown Combustion Tests Using Allison Fuel Spring Creek Coal

	AFSPC15	AFSPC16	AFSPC17	AFSPC18	AFSPC19	AFSPC20	AFSPC21	AFSPC22	AFSPC23	AFSPC24	AFSPC25
Coal Feed Rate (g/min)	0.3875	0.6028	0.3737	0.4163	0.2052	0.2145	0.3984	0.2657	0.4136	0.1833	0.4915
Total Weight Coal Fed (g)	10.1	13.0	9.0	12.8	6.1	4.0	7.0	6.4	8.5	9.5	10.6
Weight Ash Collected (g)	0.0926	0.3228	0.1244	0.6184	0.7023	0.3912	0.0330	1.7668	0.1056	0.2478	3.3245
Weight Ash Feed (g)	0.446	0.574	0.397	0.565	0.269	0.177	0.309	0.283	0.375	0.420	0.468
Percent Ash in Fly Ash (mf)	48.99	75.42	ND	31.56	18.25	17.77	4.6	10.9	56.15	89.39	6.52
Fly Ash Carbon Burnout (%)	95.0	98.4	ND	89.5	78.4	77.7	0	60.6	96.2	99.4	30.9
Avg. Feeder Air Flow Rate (slpm)	10.0	10.0	20.0	20.0	20.0	20.0	20.0	20.0	8.0	10.0	10.0
Avg. Sec. Air Flow Rate (slpm)	30.0	90.0	99.9	99.9	99.9	99.9	20.0	20.0	5.0	30.0	89.7
Avg. N ₂ Flow Rate (slpm)	39.9	99.9	99.9	99.9	99.9	99.9	40.2	40.2	13.1	39.9	99.9
Exit Gas Equivalence Ratio	0.269	0.418	0.022	0.024	0.012	0.012	0.069	0.046	0.220	0.032	0.034
% Excess Air	272	139	4524	4052	8325	7958	1348	2070	355	3041	2826
PDTF Pressure (psig)	5.2	25.6	126	132	130	128	99	92	11.6	23.0	35.7
Zone 1 Tube Temp. (°C)	1164	1259	1263	1282	1097	1382	1468	1497	1098	1098	1098
Zone 2 Tube Temp. (°C)	1253	1298	1280	1297	1098	1406	1463	1499	1098	1097	1098
Zone 3 Tube Temp. (°C)	1296	1295	955	964	840	1082	1127	1209	1096	1096	1092
Optical Zone Temp. (°C)	1035	1053	880	893	724	1029	892	905	871	909	906
Zone 4 Tube Temp. (°C)	1262	1296	921	916	866	951	898	973	1098	1097	1097
Substrate Metal Temp. (°C)	176	343	250	211	157	223	98	106	37	142	176
Prim. Gas Vel. (m/s)	7.62	3.73	2.12	2.04	2.07	2.13	2.66	2.84	4.63	4.07	3.02
Total Gas Vel. (m/s)	1.15	1.42	0.35	0.34	0.31	0.38	0.18	0.20	0.25	0.53	0.99
Accelerator Gas Vel. (m/s)	41.5	51.1	12.6	12.2	11.1	13.8	6.5	7.3	9.0	19.2	35.6
Avg. Residence Time (s)	0.35	0.28	1.1	1.2	1.3	1.0	2.2	2.0	1.6	0.75	0.40

TABLE 12

Operating Conditions and Results from Fly Ash Combustion Tests Using Allison Fuel Spring Creek Coal

	AFSPC26	AFSPC27	AFSPC28	AFSPC33	AFSPC34	AFSPC35	APSPC44	APSPC45	APSPC46
Coal Feed Rate (g/min)	0.5264	0.4016	0.4728	0.5350	0.3490	0.3794	0.3195	0.3173	0.3483
Total Weight Coal Fed (g)	10.3	8.3	16.2	20.4	14.7	11.8	17.3	16.4	18.0
Weight Ash Collected (g)	0.3037	0.1706	0.5063	0.468	3.1863	3.1104	0.3336	2.8343	4.0964
Weight Ash Feed (g)	0.454	0.367	0.715	0.901	0.649	0.521	0.764	0.724	0.795
Percent Ash in Fly Ash (mf)	ND	77.8	70.5	79.9	12.2	10.1	44.5	8.35	8.64
Fly Ash Carbon Burnout (%)	ND	98.6	98.0	98.8	65.1	57.0	94.0	47.1	49.0
Avg. Feeder Air Flow Rate (slpm)	8.0	10.0	10.0	10.0	10.0	10.0	20.0	20.0	20.0
Avg. Sec. Air Flow Rate (slpm)	5.0	30.1	30.0	30.0	30.2	30.2	20.1	20.1	20.1
Avg. N ₂ Flow Rate (slpm)	13.1	40.1	40.3	40.0	40.2	40.1	40.3	40.3	40.3
Exit Gas Equivalence Ratio	0.280	0.070	0.082	0.093	0.060	0.065	0.055	0.055	0.060
% Excess Air	257	1338	1121	979	1560	1427	1710	1723	1560
PDTF Pressure (psig)	4.3	11.2	3.2	3.9	102.9	105.8	107.8	109.6	107.8
Zone 1 Tube Temp. (°C)	1497	1484	1298	1482	1474	1298	1298	1493	1419
Zone 2 Tube Temp. (°C)	1498	1496	1298	1498	1498	1298	1298	1485	1343
Zone 3 Tube Temp. (°C)	1495	1495	1295	1496	1216	1057	1035	1156	895
Optical Zone Temp. (°C)	1182	1186	1049	1139	979	866	921	937	762
Zone 4 Tube Temp. (°C)	1320	1326	1274	1281	922	881	929	918	802
Substrate Metal Temp. (°C)	65	111	128	135	140	123	103	111	100
Prim. Gas Vel. (m/s)	6.38	5.86	8.43	8.24	1.30	1.27	2.49	2.46	2.50
Total Gas Vel. (m/s)	0.45	1.00	1.29	1.40	0.19	0.16	0.16	0.17	0.14
Accelerator Gas Vel. (m/s)	16.0	36.1	46.3	50.3	6.7	5.8	5.6	6.1	5.0
Avg. Residence Time (s)	0.90	0.40	0.31	0.29	2.15	2.47	2.55	2.37	2.86

TABLE 13

Operating Conditions from Fly Ash Combustion Tests Using
PC/AC/HWD/Micronized Spring Creek Coal

	APSPC29	APSPC32	APSPC39	APSPC40
Coal Feed Rate (g/min)	0.3742	0.1440	0.1330	0.2267
Total Weight Coal Fed (g)	18.1	13.5	13.4	11.6
Weight Ash Collected (g)	1.0076	0.5667	0.5122	0.2424
Weight Ash Feed (g)	0.799	0.596	0.592	0.512
Percent Ash in Fly Ash (mf)	13.8	20.0	46.5	58.6
Fly Ash Carbon Burnout (%)	86.7	91.5	97.6	98.5
Avg. Feeder Air Flow Rate (slpm)	10.0	9.8	20.0	20.0
Avg. Sec. Air Flow Rate (slpm)	30.0	30.0	20.2	20.2
Avg. N ₂ Flow Rate (slpm)	40.0	40.3	40.3	40.3
Exit Gas Equivalence Ratio	0.065	0.025	0.023	0.039
% Excess Air	1442	3886	4258	2456
PDTF Pressure (psig)	3.4	3.5	105.0	107.2
Zone 1 Tube Temp. (°C)	1298	1485	1298	1492
Zone 2 Tube Temp. (°C)	1298	1498	1298	1487
Zone 3 Tube Temp. (°C)	1295	1496	1027	1170
Optical Zone Temp. (°C)	1055	1167	850	903
Zone 4 Tube Temp. (°C)	1276	1307	856	862
Substrate Metal Temp. (°C)	125	140	111	124
Prim. Gas Vel. (m/s)	8.36	8.21	2.55	2.50
Total Gas Vel. (m/s)	1.27	1.42	0.16	0.17
Accelerator Gas Vel. (m/s)	45.6	51.3	5.8	6.3
Avg. Residence Time (s)	0.32	0.28	2.50	2.30

5.0 CONCLUSIONS AND FUTURE PLANS

1. Detailed chemical and mineralogic analysis for the raw and hydrothermally treated coal revealed that most of the salts of organic acid groups and soluble minerals are removed by the beneficiation process.
2. The CCSEM results indicated that although the processing into CWF reduced the total amounts of inorganic constituents present, the relative amounts of discrete minerals remained constant. That is, no significant reduction occurred in any one mineral category over another.

3. The size analysis of the CCSEM data indicates that the CWF coal was dominated by minerals in the 2.2- to 4.6-micrometer size range, while the size distribution of minerals in the raw coal was much more dispersed.
4. The changes in particle size and amounts of organically associated inorganics brought about by the beneficiation process may be important factors when considering ash behavior because they affect both the ash particle chemistry and aerodynamic behavior in the utilization system.
5. The addition of kaolin reduced the amount of sodium species present in the small size fractions ($< 1 \mu\text{m}$) by a factor of two. This indicates that the kaolin was acting as an alkali getter for the vapor-phase sodium species.
6. Beneficiation of the Spring Creek fuel by physical/acid cleaning, hot-water drying, and micronizing and just hot-water drying and micronizing both decreased the concentration of sodium species in the small size fractions. This decrease is due to the removal of significant quantities of sodium cations in the beneficiation process.
7. There is some evidence to indicate that deep cleaning the fuel might actually increase the concentration of sodium species in the small size fractions by removing inorganic species which act as effective alkali getters. Further investigation of this premise is required before solid conclusions can be made.

Further PETF testing with other beneficiated Spring Creek fuels is planned to determine the effect of the individual cleaning steps on the removal of selected inorganic species.

6.0 REFERENCES

1. Swanson, M.L.; Mann, M.D.; Moe, T.A. "Turbine Combustion Phenomena," Annual Report Contract No. DE-FC21-86MC10637, 1989, p 71.
2. Maas, D.J. et al. "Advanced Processes for Premium Low-Rank Coal/Water Fuel Production," Annual Technical Report for the Period April 1, 1987, to March 31, 1988, Prepared for the U.S. Department of Energy (DE-FC21-86MC-10637), 1988.
3. Chari, M.V. Bechtel National, "Thermal Upgrading of Low-Rank Coals, A Process Survey," Fifth Annual EPRI Contractors Conference on Coal Gasification, Palo Alto, CA, October 30-31, 1985.
4. Swanson, M.L.; Mann, M.D.; Hajicek, D.R.; Maas, D.J. "Combustion of Low-Rank Coal/Water Slurries Under Gas Turbine Operating Conditions", In Proceedings of the 13th International Conference on Coal and Slurry Technology; Denver, CO, April 12-15, 1988, pp 391-398.
5. Swanson, M.L.; Mann M.D. "Turbine Combustion Phenomena," Annual Technical Report for the Period April 1, 1987 - March 31, 1988.
6. Swanson, M.L.; Mann, M.D.; Potas, T.A. "Comparison of Coal/Water Fuels Performance in a Gas Turbine Combustor," Fourteenth Inter. Conf. on Coal & Slurry Technology, April 24-27, 1989, pp 353-364.

TABLE 14

Operating Conditions and Results from Fly Ash Combustion Tests
Using Raw Spring Creek Coal and Spring Creek Coal Mixed with
Kaolin for Alkali Gettering

	SPCRK30	SPCRK31	SPCRK37	SPCRK38	SPCRK41	SPCRK42 w/Kaol.	SPCRK43 w/Kaol.
Coal Feed Rate (g/min)	1.1835	1.0299	0.7932	0.9048	1.0122	0.5169	0.5677
Total Weight Coal Fed (g)	27.3	21.8	19.5	26.3	20.8	18.4	26.2
Weight Ash Collected (g)	1.6491	1.1468	0.3106	0.3387	0.8145	0.6004	0.1972
Weight Ash Feed (g)	1.341	1.070	0.958	1.291	1.021	1.290	1.836
Percent Ash in Fly Ash (mf)	35.2	37.2	86.8	90.4	37.0	69.5	89.2
Fly Ash Carbon Burnout (%)	90.1	90.9	99.2	99.4	90.8	96.8	99.1
Avg. Feeder Air Flow Rate (slpm)	10.0	10.0	20.0	19.3	5.0	5.0	20.0
Avg. Sec. Air Flow Rate (slpm)	30.0	30.0	20.1	20.2	0.0	0.0	20.1
Avg. N ₂ Flow Rate (slpm)	40.0	40.2	40.1	40.3	5.1	5.1	40.0
Exit Gas Equivalence Ratio	0.197	0.171	0.132	0.152	1.374	0.685	0.092
% Excess Air	408	484	660	556	0	46	987
PDTF Pressure (psig)	4.9	5.5	109.3	107.6	1.9	1.9	109.2
Zone 1 Tube Temp. (°C)	1298	1484	1498	1298	1497	1497	1498
Zone 2 Tube Temp. (°C)	1298	1498	1494	1298	1498	1498	1498
Zone 3 Tube Temp. (°C)	1295	1496	1176	1034	1495	1496	1211
Optical Zone Temp. (°C)	1039	1192	921	831	1041	1061	1053
Zone 4 Tube Temp. (°C)	1267	1321	903	938	1097	1098	981
Substrate Metal Temp. (°C)	123	132	122	96	31	30	121
Prim. Gas Vel. (m/s)	7.79	7.55	2.47	2.40	4.61	4.61	2.48
Total Gas Vel. (m/s)	1.18	1.29	0.17	0.16	0.19	0.19	0.18
Accelerator Gas Vel. (m/s)	42.4	46.5	6.2	5.6	7.0	7.0	6.3
Avg. Residence Time (s)	0.34	0.31	2.34	2.57	2.06	2.05	2.28

7. Jones, M.L.; Kalmanovitch, D.P.; Steadman, E.N.; Benson, S.A.
"Application of SEM Techniques to the Characterization of Coal and Coal
Ash Products," H.L.C. Meuzelaar, Ed., *Advances in Coal Spectroscopy*,
1992, p 1-27.
8. Kalmanovitch, D.P.; Montgomery, G.G.; Steadman, E.N. ASME Paper Number
87-JPGC-FACT-4, 1987.
9. Steadman, E.N.; Benson, S.A.; Zygarlicke, C.J.; Brekke, D.W.
"Characterization of Liquid Phase Components in Coal Ashes and Deposits,"
*In Proceedings of the Seventh Annual International Pittsburgh Coal
Conference; September 14-18, 1990.*

TABLE 15
SEMP and XRD Analyses--Multicyclone Fly Ash Samples

Run #:	SPCRK037	SPCRK037	SPCRK037			
Collection Device:	Cyclone #2	Cyclone #5	Final Filter			
Fuel Type:	Spring Creek	Spring Creek	Spring Creek			
Sample Weights (g)	0.2558	0.0225	0.0323			
Particle Size by Malvern 2600						
Sample Mean Size (μm)	15.4	19.5	60.3			
Sample Top Size (99%<, μm)	72.2	119.8	420.0			
Total Number of Points	293	249	249			
Particle Types, % of Total Counts						
Crystalline Phases						
Akermanite	0.7	0.0	0.0			
Gehlenite	2.0	1.6	0.0			
Anorthite	1.4	0.0	0.0			
Albite	1.0	0.0	0.0			
Nepheline	0.3	0.0	0.0			
Pyroxene	0.3	0.0	0.0			
Spurrite	0.0	0.4	0.0			
Calcium Aluminate	4.4	1.2	0.0			
Quartz	33.8	0.4	0.0			
Iron Oxide	0.7	0.0	0.0			
Ankerite (Ca, Mg, Fe)CO ₃	0.3	0.0	0.0			
Aluminum Oxide	0.3	0.0	0.0			
Dolomite	1.4	0.0	0.0			
Barite	0.3	0.4	0.0			
Sodium Sulfate	0.0	0.0	7.6			
Unclassified and Amorphous Phases						
Unclassified	32.8	95.6	92.4			
Pure Kaolinite (Amorp.)	13.0	0.0	0.0			
Kaolinite-Derived	4.1	0.4	0.0			
Illite (Amorp.)	0.7	0.0	0.0			
Montmorillonite (Amorp.)	2.0	0.0	0.0			
Calcium-Derived	0.3	0.0	0.0			
Average Composition (wt%)	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>
SiO ₂	56.8	42.1	12.5	12.6	1.0	5.6
Al ₂ O ₃	17.6	27.5	22.6	23.6	0.6	2.9
Fe ₂ O ₃	3.9	4.7	11.8	12.3	2.9	4.1
TiO ₂	1.1	1.6	2.1	2.1	0.1	0.0
P ₂ O ₅	0.1	0.1	0.4	0.4	0.2	0.6
CaO	12.7	15.3	34.9	36.2	3.5	5.0
MgO	3.5	3.8	8.9	9.4	2.0	3.3
Na ₂ O	3.2	4.5	3.1	3.3	43.5	73.1
K ₂ O	0.3	0.4	0.1	0.1	2.9	5.4
SO ₃	0.7	0.0	3.5	0.0	43.4	0.0
X-Ray Diffraction Results						
Quartz, SiO ₂	Major		NA		ND	
Mullite, Al ₂ Si ₂ O ₇	Minor		NA		ND	
Cristobalite, SiO ₂	Minor		NA		ND	
Lime, CaO	Minor		NA		ND	
Periclase, MgO	Minor		NA		ND	
Sodium Sulfate, Na ₂ SO ₄	ND		NA		Major	
Iron Silicide, Fe ₂ Si	ND		NA		Major	

TABLE 16

SEMPC and XRD Analyses--Multicyclone Fly Ash Samples Run APSPC040

Run #:	APSPC040	APSPC040	APSPC040			
Collection Device:	Cyclone #2	Cyclone #5	Final Filter			
Cleaning:	Acid/Physical	Acid/Physical	Acid/Physical			
Fuel Type:	Spring Creek	Spring Creek	Spring Creek			
Sample Weights (g)	0.1934	0.0235	0.0255			
Particle Size by Malvern 2600						
Sample Mean Size (μm)	15.1	10.4	30.7			
Sample Top Size (99%<, μm)	77.5	46.3	130.5			
Total Number of Points	248	248	102			
Particle Types, % of Total Counts						
Crystalline Phases						
Gehlenite	2.0	0.0	0.0			
Anorthite	6.5	0.8	0.0			
Albite	3.6	0.8	0.0			
Nepheline	0.4	0.8	0.0			
Pyroxene	0.4	0.4	0.0			
Mullite	0.4	0.0	0.0			
Spurrite	0.4	0.0	0.0			
Häüyne	0.4	0.8	0.0			
Spinel	0.4	0.0	0.0			
Quartz	13.3	2.0	0.0			
Iron Oxide	1.2	0.0	0.0			
Calcium Oxide	0.8	0.0	0.0			
Sodium Sulfate	0.4	0.0	1.0			
Sodium Calcium Sulfate	0.4	0.4	0.0			
Unclassified and Amorphous Phases						
Unclassified	48.0	90.3	99.0			
Pure Kaolinite (Amorp.)	10.5	0.0	0.0			
Kaolinite-Derived	5.6	3.2	0.0			
Montmorillonite (Amorp.)	5.2	0.4	0.0			
Average Composition (wt%)	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>
SiO ₂	45.2	41.3	24.2	23.6	5.3	8.8
Al ₂ O ₃	25.4	31.8	32.5	35.9	6.5	11.5
Fe ₂ O ₃	5.1	5.2	14.4	14.8	15.2	21.4
TiO ₂	1.3	1.3	2.0	2.3	0.3	0.6
P ₂ O ₅	0.1	0.1	0.4	0.5	1.9	2.6
CaO	9.6	10.2	9.2	10.1	1.9	3.2
MgO	3.2	4.0	4.4	4.8	6.5	9.2
Na ₂ O	5.0	5.6	7.2	7.6	39.3	40.6
K ₂ O	0.3	0.4	0.2	0.4	1.3	2.0
SO ₃	4.8	0.0	5.4	0.0	21.8	0.0
X-Ray Diffraction Results	Not Available					

10. Steadman, E.N.; Erickson T.A. "Coal and Ash Characterization--Digital Image Analysis Applications," Engineering Foundation Conference, Inorganic Transformations and Ash Deposition During Combustion, Palm Coast, FL, March 10-15, 1991.
11. Benson, S.A.; Holm, P.L. "Comparison of the Inorganic Constituents in Low-Rank Coals," *Ind. Eng. Chem. Prod. Res. Dev.* 1985, 24, 145.

TABLE 17

SEMPC and XRD Analyses--Multicyclone Fly Ash Samples Run SPCRK041

Run #:	SPCRK041	SPCRK041	SPCRK041			
Collection Device:	Cyclone #2	Cyclone #5	Final Filter			
Fuel Type:	Spring Creek	Spring Creek	Spring Creek			
Sample Weights (g)	0.7201	0.0584	0.0360			
Particle Size by Malvern 2600						
Sample Mean Size (μm)	30.4	9.6	54.6			
Sample Top Size (99%<, μm)	509.0	77.5	161.1			
Total Number of Points	85	249	252			
Particle Types, % of Total Counts						
Crystalline Phases						
Gehlenite	1.2	4.0	0.0			
Anorthite	4.7	1.2	0.0			
Calcium Aluminate	3.5	2.0	0.0			
Quartz	27.1	0.0	0.0			
Iron Oxide	0.0	0.4	0.0			
Calcium Oxide	2.4	2.4	0.0			
Ankerite (Ca, Mg, Fe)CO ₃	1.2	0.4	0.0			
Dolomite	0.0	0.4	0.0			
Barite	1.2	0.0	0.0			
Sodium Sulfate	0.0	0.0	5.2			
Sodium Calcium Sulfate	1.2	0.4	1.6			
Unclassified and Amorphous Phases						
Unclassified	42.4	88.4	93.3			
Pure Kaolinite (Amorp.)	5.9	0.0	0.0			
Kaolinite-Derived	8.2	0.4	0.0			
Montmorillonite (Amorp.)	1.2	0.0	0.0			
Average Composition (wt%)	Bulk	Amorphous	Bulk	Amorphous	Bulk	Amorphous
SiO ₂	49.7	37.8	20.7	22.2	2.4	6.1
Al ₂ O ₃	19.7	27.5	23.1	24.0	1.9	4.6
Fe ₂ O ₃	4.5	5.7	8.9	9.2	2.1	4.8
TiO ₂	1.3	2.1	1.3	1.3	0.2	0.4
P ₂ O ₅	0.1	0.1	0.2	0.2	0.2	0.6
CaO	16.2	17.1	32.3	31.5	5.2	11.7
MgO	3.8	5.2	8.2	8.2	1.1	2.4
Na ₂ O	3.2	4.1	3.2	3.3	31.9	66.4
K ₂ O	0.2	0.3	0.1	0.1	1.6	2.9
SO ₃	1.3	0.0	2.1	0.0	53.3	0.0
X-Ray Diffraction Results						
Quartz, SiO ₂	Minor		Minor		Minor	
Lime, CaO	ND		Minor		ND	
Periclase, MgO	ND		Minor		ND	
Sodium Sulfate, Na ₂ SO ₄	ND		ND		Minor	
Bredigite, Ca ₂ Mg ₂ (SiO ₄) ₂	ND		ND		Minor	

TABLE 18

SEMP and XRD Analyses--Multicyclone Fly Ash Samples Run SPCRK042

Run #:	SPCRK042		SPCRK042		SPCRK042	
Collection Device:	Cyclone #2		Cyclone #5		Final Filter	
Fuel Type:	Spring Creek w/ Kaolin		Spring Creek w/ Kaolin		Spring Creek w/ Kaolin	
Sample Weights (g)	0.4716		0.1125		0.0163	
Particle Size by Malvern 2600						
Sample Mean Size (μm)	32.8		20.9		83.2	
Sample Top Size (99% $\leq$, μm)	461.8		108.3		370.3	
Total Number of Points	249		249		249	
Particle Types, % of Total Counts						
Crystalline Phases						
Gehlenite	12.4		9.6		0.0	
Anorthite	5.2		22.5		0.0	
Albite	0.4		0.0		0.0	
Nepheline	0.0		0.0		0.4	
Mullite	0.0		0.4		0.0	
Häüyne	0.4		0.0		0.4	
Calcium Aluminate	1.6		0.0		0.0	
Quartz	9.2		0.0		0.0	
Iron Oxide	0.4		0.0		0.0	
Calcium Oxide	1.2		0.4		0.0	
Aluminum Oxide	0.4		0.0		0.0	
Rutile	0.4		0.0		0.0	
Dolomite	0.4		0.0		0.0	
Barite	0.3		0.0		0.0	
Anhydrite	1.2		0.0		0.0	
Sodium Calcium Sulfate	0.8		0.0		0.4	
Ferric Sulfate	0.4		0.0		0.0	
Unclassified and Amorphous Phases						
Unclassified	31.3		55.8		98.8	
Pure Kaolinite (Amorp.)	18.1		0.0		0.0	
Kaolinite-Derived	12.9		10.8		0.0	
Illite (Amorp.)	0.4		0.0		0.0	
Montmorillonite (Amorp.)	2.4		0.4		0.0	
					0.0	
Average Composition (wt%)	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>
SiO ₂	42.2	42.2	34.6	33.5	11.6	18.6
Al ₂ O ₃	27.9	32.9	32.8	32.4	9.9	15.9
Fe ₂ O ₃	3.7	3.2	4.3	4.7	2.7	4.5
TiO ₂	1.6	1.4	1.7	1.9	1.0	1.6
P ₂ O ₅	0.3	0.5	0.2	0.4	0.7	1.1
CaO	14.5	12.1	15.8	17.0	5.9	9.6
MgO	3.3	3.0	4.0	4.4	1.7	2.8
Na ₂ O	3.8	4.4	5.7	5.5	25.7	42.5
K ₂ O	0.3	0.3	0.2	0.2	2.1	3.4
SO ₃	2.5	0.0	0.6	0.0	38.7	0.0
X-Ray Diffraction Results						
Quartz, SiO ₂	Minor		Major		Minor	
Anhydrite, CaSO ₄	ND		ND		Minor	
Pyrrhotite, Fe _{1-x} S	ND		ND		Minor	

TABLE 19

SEMP and XRD Analyses--Multicyclone Fly Ash Samples Run SPCRK043

Run #:	SPCRK043	SPCRK043	SPCRK043			
Collection Device:	Cyclone #2	Cyclone #5	Final Filter			
Fuel Type:	Spring Creek w/ Kaolin	Spring Creek w/ Kaolin	Spring Creek w/ Kaolin			
Sample Weights (g)	0.1572	0.0322	0.0078			
Particle Size by Malvern 2600						
Sample Mean Size (μm)	15.5	8.6	36.4			
Sample Top Size (99%<, μm)	64.4	101.4	148.0			
Total Number of Points	249	249	249			
Particle Types, % of Total Counts						
Crystalline Phases						
Gehlenite	10.8	5.6	0.0			
Anorthite	4.8	7.2	0.0			
Albite	0.4	0.0	0.0			
Nepheline	0.8	0.4	0.0			
Häüyne	0.4	0.4	0.0			
Quartz	8.0	0.0	0.0			
Iron Oxide	0.4	0.0	0.0			
Calcium Oxide	0.4	0.0	0.0			
Barite	1.2	0.0	0.0			
Sodium Sulfate	0.0	0.0	8.8			
Unclassified and Amorphous Phases						
Unclassified	43.8	83.5	91.2			
Pure Kaolinite (Amorp.)	19.3	0.0	0.0			
Kaolinite-Derived	8.0	2.8	0.0			
Montmorillonite (Amorp.)	1.6	0.0	0.0			
Average Composition (wt%)	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>
SiO ₂	41.8	39.1	28.5	27.8	2.9	6.2
Al ₂ O ₃	29.7	33.2	30.5	30.5	1.7	4.0
Fe ₂ O ₃	3.7	3.6	6.3	6.8	2.0	3.5
TiO ₂	1.2	1.4	2.1	2.2	0.2	0.4
P ₂ O ₅	0.1	0.1	0.5	0.6	0.7	1.3
CaO	14.1	14.1	19.2	20.2	4.0	7.4
MgO	3.2	3.1	5.4	5.6	1.8	3.3
Na ₂ O	4.7	5.1	6.2	6.1	42.5	68.8
K ₂ O	0.3	0.3	0.1	0.1	2.8	4.9
SO ₃	1.3	0.0	1.2	0.0	41.4	0.0
X-Ray Diffraction Results						
Quartz, SiO ₂	Minor		Minor		ND	
Mullite, Al ₄ Si ₂ O ₁₁	Minor		ND		ND	
Periclase, MgO	Minor		Minor		ND	
Pyrrhotite-6C, Fe _{1-x} S	Minor		ND		ND	
Iron Silicide, Fe ₂ Si	ND		ND		Minor	
Sodium Sulfate, Na ₂ SO ₄	ND		ND		Major	
Ferrite Spinel, (Mg, Fe)(Fe, Al) ₂ O ₄	ND		Minor		ND	

TABLE 20

SEMP and XRD Analyses--Multicyclone Fly Ash Samples Run AFSPC045

Pin #:	AFSPC045	AFSPC045	AFSPC045			
Collection Device:	Cyclone #2	Cyclone #5	Final Filter			
Fuel Type:	Allison Fuel Spring Creek	Allison Fuel Spring Creek	Allison Fuel Spring Creek			
Sample Weights (g)	2.1765	0.0768	0.5810			
Particle Size by Malvern 2600						
Sample Mean Size (μm)	19.9	18.6	10.6			
Sample Top Size (99%<, μm)	131.9	48.1	68.2			
Total Number of Points	51	40	169			
Particle Types, % of Total Counts						
Crystalline Phases						
Gehlenite	9.8	7.5	0.6			
Anorthite	0.0	0.0	1.8			
Albite	0.0	2.5	0.0			
Calcium Aluminate	0.0	2.5	0.0			
Quartz	17.6	40.0	0.6			
Iron Oxide	2.0	2.5	0.0			
Pyrite	2.0	0.0	0.0			
Unclassified and Amorphous Phases						
Unclassified	52.9	25.0	92.3			
Pure Kaolinite (Amorp.)	5.9	17.5	2.4			
Kaolinite-Derived	5.9	0.0	2.4			
Illite (Amorp)	2.0	0.0	0.0			
Montmorillonite (Amorp.)	2.0	2.5	0.0			
Average Composition (wt%)	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>	<u>Bulk</u>	<u>Amorphous</u>
SiO ₂	38.6	29.9	70.0	46.3	9.1	27.7
Al ₂ O ₃	20.9	27.7	15.1	33.1	7.8	27.1
Fe ₂ O ₃	4.8	3.6	0.5	0.0	4.0	4.4
TiO ₂	1.3	1.9	0.4	0.9	0.2	0.5
P ₂ O ₅	0.1	0.1	0.1	0.2	0.8	0.5
CaO	17.1	20.8	8.3	14.5	6.6	14.6
MgO	5.7	7.1	1.8	2.8	8.7	7.6
Na ₂ O	5.8	8.4	1.8	2.2	37.3	17.1
K ₂ O	0.4	0.5	0.0	0.0	1.2	0.5
SO ₃	5.2	0.0	2.1	0.0	24.3	0.0
X-Ray Diffraction Results	Not Available					

12. Nowok, J.W.; Benson, S.A.; Jones, M.L.; Kalmanovitch, D.P. "Sintering Behavior and Strength Development in Various Coal Ashes," *Fuel* 1990, 69, 1020-1029.
13. Wenglarz, A.; Ames, F.; Fox, R.; Wilkes C.; Williams, J. "Gas Turbine Screening Program," final report for DOE Contract DOE/MC/21394-2199 (DE87001057), December 1986, 85 p.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORTFORM APPROVED
OMB NO. 1800-0127
Page 1 of 2

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Turbine Combustion Phenomena (3.1)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-86
		6. Completion Date 9-30-92

11. Major Milestone Status	Units Planned	Units Complete
A. Revised Technology and Market Assessment	P	C
B. Characterization of LRCs' Atomization Properties	P	C
C. Evaluation of LRC Fuel Agglomeration	P	C
D. Investigation of Particulate Hot-Gas Cleanup Systems	P	C
E-1. Ash Transformation Studies for Beneficiated LRC Fuels	P	C
E-2. PDTF Additive Testing for Improved Ash Characteristics	P	C
F. Investigation of Slagging Combustor Design	P	C
G. Baseline Combustion Test with Spring Creek Fuel Utilized in GM Allison Combustion Tests	P	C
H. Final Report	P	C

12. Remarks

Due to EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date

Michael J. Johnson 7-29-92-

14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Turbine Combustion Phenomena (3.1)		3. Reporting Period 4-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Revised Technology and Market Assessment -- Completed in Year 4 --				
Task B	Characterization of LRCs' Atomization Properties -- Completed in Year 5 --				
Task C	Evaluation of LRC Fuel Agglomeration -- No activities in Year 6 --				
Task D d.1	Investigation of Particulate Hot-Gas Cleanup Systems: Design and construct ceramic barrier filter probes for conducting long-term testing in the pressurized drop-tube furnace (PDTF)	1-31-92			
d.2	Conduct two long-term ceramic barrier filter tests to examine filter performance and ceramic material degradation.	6-15-92			
Task E E-1.1	Ash Transformation Studies: Perform ash transformation studies for beneficiated LRC fuels.	1-31-92		Moved back due to other project use of PDTF	
E-2.1	Construct slurry droplet feed system for PDTF.	10-31-91			
E-2.2	Perform additive testing for improved ash characteristics.	1-31-92		Moved back due to other project use of PDTF	
Task F	Investigation of Slagging Combustor Design -- No work planned for Year 6 --				
Task G	Baseline Combustion Test with Spring Creek Fuel Utilized in GM Allison Combustion Tests	2-29-92			
Task H	Final Report	8-31-92			

3.2 Combustion Inorganic Transformation

COMBUSTION INORGANIC TRANSFORMATIONS

Annual Technical Progress Report
for the Period January 1, 1991 - June 30, 1992

by

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July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

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COMBUSTION INORGANIC TRANSFORMATIONS

1.0 EXECUTIVE SUMMARY

1.1 Task 1: Prediction of Fly Ash Particle Size and Composition

Two models have been developed to predict fly ash particle size and composition from initial coal composition: 1) a stochastic model, "ATRAN1," which combines coal inorganics in a random manner and outputs a predicted fly ash particle size and composition; and 2) an expert system model, "ASHPERT," which gives a first-order estimate of fly ash size and composition, relying heavily on a large empirical database. Both models input data obtained through computer-controlled scanning electron microscopy (CCSEM), chemical fractionation, bulk elemental composition, and proximate analyses.

The stochastic model ATRAN1 has been modified and automated. It is used to predict the partitioning of inorganics during combustion and incorporates a mass balancing algorithm to extend its use to lower-rank coals. Three coals were used for testing and modification of the existing model: Eagle Butte, Kentucky #9, and a blend of Eagle Butte (70%) and Kentucky #9 (30%). The predicted Eagle Butte fly ash contained a larger amount of nucleated submicron particles due to the large amount of organically associated constituents present in the coal. Experimental fly ash produced using particle residence times and temperatures associated with fouling and slagging conditions in a boiler was generated from the coals in order to compare experimental and predicted fly ash composition and size. Slagging conditions include shorter particle residence times and higher gas temperatures at the point of collection than fouling conditions. The CCSEM mineral phase composition of the experimental blend fly ash compared fairly well with that of the predicted compositions. Particle-size distributions (PSD) of the experimental and predicted fly ash also compared fairly well.

The ASHPERT database was increased to include 45 coals and ashes. The fly ash included in the ASHPERT database no longer needs to be exclusively drop-tube furnace (DTF)-generated, but can also originate from pilot- or full-scale combustion sources. Also included for each coal in ASHPERT is proximate/ultimate and chemical fractionation data (if a low-rank coal). X-ray fluorescence (XRF) elemental composition data are also included for both the coal and the fly ash. The mineral particle-type classification program MINER has also been incorporated into ASHPERT. This addition considerably enhances the applicability of ASHPERT in other areas of combustion modeling.

1.2 Task 2: Laboratory-Scale Combustion Testing

A synthetic coal containing pyrite and kaolinite was produced and combusted in the Energy and Environmental Research Center (EERC) DTF. Fly ash was collected and analyzed using CCSEM to examine interactions between mineral species. The results for previous sodium-silica-sulfur and calcium-silica-sulfur are presented along with the pyrite-kaolinite system data. The results obtained are as follows:

- The Na(org.)-Si-S system exhibits interaction between species at 900°C to produce sodium sulfate-silicate phases; above 900°C, silica

dominates due to the loss of sodium and sulfur by devolatilization and decomposition. The PSD of the fly ash decreased with increasing temperature as the result of either char fragmentation or the loss of low melting point sodium silicate or sulfate species which tend to "glue" or cause coalescence of the ash particles.

- The Ca(org.)-Si-S and Ca(min.)-Si-S systems exhibit interactions, primarily between calcium and silica, throughout the 900° to 1500°C temperature range. Unlike the Na(org.)-Si-S system, the calcium-containing system exhibited increased levels of Ca silicates with increasing temperatures. This is primarily due to the lower volatility of calcium as compared to sodium, allowing for more calcium to be retained on the char particle during combustion. Some anhydrite was formed, but was probably the result of SO₂ reacting with the surface of the calcium or quartz grains in the cooling zone of the ash quench probe. Particle agglomeration was seen at the highest temperature studied for the Ca(org.)-Si-S and Ca(min.)-Si-S systems.
- Interaction between ash components occurs over a broader temperature range for calcium-containing ash than for organic sodium-containing ashes. However, softening and rounding of the particles occur at lower temperatures for the sodium-containing ash.
- An enhanced rate of carbon conversion was observed for the Ca(org.)-Si-S over that of the Ca(min.)-Si-S at 900°C. This is in agreement with previous studies showing the catalytic effect of organically-bound calcium during combustion.
- The Ca(org.)-Si-S and Ca(min.)-Si-S systems give generally similar compositional diagrams over the temperature range examined, except for the scarcity of calcium-sulfur species in the Ca(org.)-Si-S system.
- The Fe(min.)-Al-Si system loses nearly all the sulfur from the pyrite at 900°C, leaving kaolinite and iron oxide. The system shows only a small degree of interaction between the kaolinite and iron until 1500°C, when an increased amount of iron aluminosilicate components form.

Combustion testing in the EERC DTF was completed for an Eagle Butte (70%)/Kentucky #9 (30%) coal blend. Approximately 1000 pounds of blended coal was prepared. Coal analyses revealed that the blending operation was quite successful since the physical and chemical parameters measured for the blend are each equivalent to weighted averages of the components in the parent coals. The blend was combusted in the DTF at a gas temperature of 1500°C. Short residence time chars and a carbon-free fly ash were produced in the DTF. Fly ash that was generated from the Eagle Butte/Kentucky #9 blend was collected on a bulk filter and also aerodynamically size-segregated in a six-stage multicyclone. The fly ash revealed very little interaction between the mineral components of the two different coals. Viscosity distributions of liquid phases in the fly ash under slagging conditions for the blend were intermediate between that of a weighted average of the parent fly ashes and the Kentucky #9. The base deposit of the blend grown under slagging conditions was effectively the same as that of the Kentucky #9. Viscosity distributions of the main portion of the deposits grown under fouling

conditions were similar for the blend and the parent coals. Iron-rich particles derived from the pyrite in the Kentucky #9 coal experienced only limited interaction with aluminosilicates, most of which had sources in the Kentucky #9.

1.3 Task 3: Development of Analytical Methods

A round-robin CCSEM analysis has been initiated involving the following seven laboratories: EERC, Ames Laboratory at Iowa State University, Sandia National Laboratory, the University of Kentucky, the R.J. Lee Group, the Netherlands Energy Research Center, and CSIRO of Australia. In order to design the round-robin, information was gathered from each of the participating domestic laboratories regarding their CCSEM systems. The EERC then prepared a detailed protocol describing scanning electron microscopy (SEM) system configuration for analysis of standard coals and sent the protocol together with sample sets to the participating laboratories. Three Argonne National Laboratory premium coals are being considered for round-robin use including Illinois #6, Pittsburgh #8, and Wyodak. The results of the round-robin testing will be used to initiate standardization of the CCSEM technique.

A correction for improving the accuracy of CCSEM elemental compositions was devised. This procedure involves the extraction of k-ratios during acquisition of raw CCSEM data, followed by correction of these k-ratios for atomic number (Z), absorption (A), and fluorescence (F) effects. This is called a ZAF correction and results in more accurate quantitative chemistries of individual fly ash particles or coal minerals. Three bituminous coals and five ashes were analyzed using the CCSEM-ZAF technique. To determine the accuracy of the CCSEM-ZAF technique, coal and ash compositions determined through CCSEM were compared to bulk compositions as measured using XRF. Results indicate the CCSEM-ZAF data require corrections for Ca, Mg, and Si, because these elements occur in significant concentrations in the submicron-size fraction. In the future, appropriate corrections will be made using results obtained through mass balance calculations and through analysis of individual submicron particles. These two techniques are described separately below.

Particle-by-particle scanning electron microscope (PBPSEM) analysis has been refined into a fully automated technique. It uses advanced image analysis together with the standard CCSEM procedure to yield the size and composition of coal minerals on an individual particle basis. PBPSEM greatly enhances ash formation and deposition models by providing much more comprehensive coal input data. The PBPSEM program uses completely automated digital image acquisition, processing, and image segmentation. This is a major advance over the semiautomated program described earlier (1). In PBPSEM, the major operating parameter affecting the sizing and location of particles is the determination of the difference between coal and minerals in the grey-level histogram. The method currently used for determining this difference works well for homogeneous systems. The present emphasis is on developing a technique to evaluate the reproducibility of grey-level histograms in heterogeneous coal systems and also on developing ways of improving the distinction between the different components in the system. Testing of the PBPSEM method continues, with the goal of expanding its applicability.

A method has been devised to balance the mass of organically and mineralogically associated inorganics in coal so that their sum equals the total ash content of the coal. An algorithm to determine the distribution of organically associated inorganics was created using CCSEM, chemical fractionation, and XRF data. The inorganics are divided into soluble minerals, insoluble minerals, organically associated inorganics, and insoluble submicron minerals. The technique was modified to better estimate the amount of submicron silica. The mass balancing technique was tested on the Kentucky #9, Eagle Butte, and Kentucky #9/Eagle Butte blend coals. Kentucky #9 contained little organically associated material, whereas the Eagle Butte coal had large amounts of organically associated calcium and magnesium. The quantity of organically bound material in the Kentucky #9/Eagle Butte blend was intermediate between that of the two parent coals.

A new technique, termed scanning electron microscopy with image analysis (SEM-IA), was developed for analysis of individual submicron ash particles. SEM-IA provides data similar to that of the CCSEM technique for 1- to 100- μm -diameter particles. A freeze-dried dispersion method was developed as an alternative sample preparation technique. Using this method, ash particles are suspended in propanol and dispersed onto pieces of vitreous carbon measuring approximately 1 cm^2 . Freeze-drying maintains an adequate separation between particles, as required for SEM-IA. During analysis, size measurements of the individual particles are not made in real time as they are in CCSEM, but only after a large number of duplicate images of a sample field of view have been acquired and averaged to remove noise. This additional image processing step is necessary to obtain accurate size measurements for the smallest particles. The image-averaging ability of the SEM-IA technique provides size and composition distribution data for particles with diameters an order of a magnitude smaller than those that can be analyzed by CCSEM, or approximately 0.1- μm minimum diameter.

2.0 GOALS AND OBJECTIVES

The aim of this project was to achieve an overall understanding of the physical and chemical changes that occur in the inorganic matter of coal during combustion by developing a means to predict the state (vapor, liquid, or solid), composition, and size of the inorganic material at any point in a combustion system, given the coal composition and combustion conditions. The work was divided into three tasks.

Task 1 involved developing expert systems to predict fly ash composition and size from initial coal characteristics using two approaches. The first is a stochastic model, "ATRAN1," that simulates the coalescence, fragmentation, and decomposition of initial coal minerals during their transformation to fly ash particles. The second model, "ASHPERT," produces a first-order estimate of fly ash size and composition that can easily be integrated with other expert systems. Data for use in ASHPERT were generated in the Pittsburgh Energy Technology Center (PETC) mineral matter programs at the EERC for 45 test coals and ashes. Inorganic components were measured for the coals and ashes. CCSEM and chemical fractionation were used to determine the association, size, composition, and juxtaposition of the inorganic components. All of these data are used by ASHPERT to predict the size and composition of ash particles based on coal composition and combustion conditions.

Task 2 involves laboratory-scale testing of the physical and chemical changes of inorganic phases during combustion. Chars and ashes were examined to determine their bulk composition, phase distribution, and morphology. Data were obtained using SEM and electron microprobe analysis (EMA), XRF, and x-ray diffraction (XRD). The goal was to track the transformation of inorganic constituents of representative coals at various degrees of coal particle burnout until fly ash was produced. The DTF system was used to produce chars at various degrees of burnout and, ultimately, a carbon-free fly ash. Model mineral/coal mixtures were also produced and combusted to examine some of the transformations in detail. The database generated in this task was used to formulate the predictive models described under Task 1.

Task 3 involves development of CCSEM methods for determining the size, composition, and juxtaposition of mineral grains in pulverized coals. An additional aspect of this task is the extension of CCSEM methods to submicron minerals and fly ash particles. Proper determination of the inorganic components in coal is an essential requirement in understanding and ultimately predicting the transformations of inorganic components during coal combustion. To obtain a more complete understanding of the coal compositions, chemical fractionation was used to measure the abundance of organically associated inorganic constituents in the lower-rank subbituminous and bituminous coals.

During the past three years, the project has focused on developing consistent and quantitative techniques for analyzing the inorganic components of coals, chars, and fly ash. This emphasis is essential because the fate of inorganic matter during combustion cannot be predicted accurately without the availability of consistent and reliable data. In conjunction with the above three tasks is an ongoing effort to evaluate all data for precision and accuracy. A further goal of the quality control effort is to obtain fully quantitative, standardized data. Quality-control measures were applied to coal and ash characterization data as well as to char and fly ash formation tests in the DTF.

2.1 Task 1: Prediction of Fly Ash Particle Size and Composition

The objectives of the fly ash particle size and composition prediction task were as follows:

1. Develop an algorithm which will allow for the addition of organically bound inorganics to the stochastic model ATRAN1.
2. Characterize coal inorganics in Eagle Butte, Kentucky #9 and Eagle Butte/Kentucky #9 blend coals using CCSEM and chemical fractionation. These data were used to operate the mechanistic stochastic model for fly ash particle size and composition prediction.
3. Generate experimental fly ash under slagging and fouling conditions for comparison with stochastic predictions.
4. Enhance the ASHPERT database to include CCSEM data for 45 coals and corresponding fly ash samples. Include additional information such as XRF and proximate/ultimate data.

2.2 Task 2: Laboratory-Scale Combustion Testing

The objectives of the laboratory-scale combustion testing were as follows:

1. Production, characterization and combustion testing of synthetic coal/char model mixtures for the purpose of studying inorganic transformations in systems limited in inorganic constituents. The systems studied included:
 - a. Sodium-silica-sulfur (simulation of organically bound Na).
 - b. Calcium-silica-sulfur (simulation of organically bound Ca).
 - c. Calcium-silica-sulfur (mineral-bound Ca as calcite).
 - d. Iron-aluminosilicate (using pyrite and kaolinite).
2. Combust well-characterized Eagle Butte and Kentucky #9 parent coals and a 70% Eagle Butte/30% Kentucky #9 blend in order to determine the transformations of inorganic components.

2.3 Task 3: Development of Analytical Methods

The objectives of the analytical methods development task during this year were as follows:

1. Begin an interlaboratory round-robin CCSEM analysis of prepared coal samples.
2. Evaluate the accuracy of the ZAF correction method for CCSEM data.
3. Develop a PBPSEM, a new CCSEM method which uses image analysis to characterize coal minerals on a particle-by-particle basis.
4. Determine the amount of mineral versus organically bound inorganic matter in three coals using a mass balancing procedure.
5. Extend automated SEM analysis methods to submicron particles, and evaluate by comparison with standard CCSEM results.

3.0 TASK 1: Prediction of Fly Ash Particle Size and Composition

3.1 Introduction

The key to developing a model to predict the composition and size of fly ash is a well-established database of coal mineral and corresponding fly ash data for coals of varied ranks. In order to understand the physical and chemical transformations that occur during combustion, it is particularly important to have sufficient quantitative data on the inorganic content of coal and fly ash. Mineral and ash characterization results were used to establish a foundation for model development and verification. Data were obtained using SEM and electron microprobe techniques along with standard inorganic analysis.

3.2 Equipment and Procedures

Most of the characterization of coal minerals and the corresponding ash was performed using CCSEM. The technique is discussed below in the section on Task 3, Development of Analytical Methods. CCSEM yields size and composition information for discrete minerals and ash particles. Chemical fractionation was used to measure the finely dispersed minerals and organically bound inorganics that are beyond the detection limits of the SEM (2). Another technique used for analyzing just the fly ash is scanning electron microscopy point count (SEMP), which yields ZAF-corrected chemistries, but does not include size data. The method and accessory data-processing software were developed at the EERC. SEMPC involves microprobe analysis of about 250 random points in a polished cross-sectioned sample and is used to determine the relative abundance of phases in ashes and deposits (3). Data for each point are transferred to a computer file for later processing, including calculation of molar and weight ratios of elements. Using these ratios, points with compositions of known phases (common to ashes and coal minerals) are identified and counted. The software also determines the proportion of unknowns, those for which there are no known phases corresponding to the chemical composition. For this study, it was assumed that the unknown phases were amorphous. The average chemistry of all points is calculated for each sample in order to obtain a bulk composition.

3.3 Predictive Model for Fly Ash Size and Composition

3.3.1 Introduction

Two models have been developed at the EERC for use in predicting fly ash particle size and composition from CCSEM analyses of coal. Both models are phenomenological, requiring detailed coal input data and empirically derived knowledge of inorganic transformation phenomena occurring during combustion. The first model, "ATRAN1," is stochastic and simply combines initial coal inorganics in a random manner in order to predict the resultant fly ash particle size and composition. The acronym is derived by shortening the phrase "ash transformation" and adding the number "1" to indicate future refinements and modifications of the code. ATRAN1 is considered stochastic because it randomly combines data from coal mineral analyses to produce predictions of fly ash compositions. The model does not operate in a completely random manner in that associations among coal minerals (i.e., locked vs. liberated) influence the predictions. The second model, "ASHPERT," is an expert system yielding a first-order estimate of fly ash size and composition. Both models are designed to emulate pulverized coal combustion and, hence, use data derived from coals ground to 70%-80% -200 mesh.

3.3.2 Experimental

Both ATRAN1 and ASHPERT use CCSEM data as their primary input regarding the identity, chemistry, size, quantity, and mineral-to-coal association (locked or liberated) of the minerals. Data are required on an individual-particle basis in order to model transformations and interactions between individual minerals locked within and liberated from coal particles. CCSEM data provide all of the above parameters for minerals greater than 1 μm in average diameter, whereas chemical fractionation results are used for information on organically bound inorganics or minerals less than 1 μm in size.

Fly ash was generated in a vertical laminar-flow furnace (DTF) for comparison with the predicted fly ash. The DTF is a laboratory-scale furnace system that simulates conditions in commercial combustors without the high cost associated with pilot-scale combustion testing. The combustion tests for the work reported here were performed using slagging and fouling conditions which include gas temperatures of 1500°C, particle residence times of 1-3 seconds, an oxygen atmosphere of about 21%, and a filter trap to collect bulk ash. Fouling conditions involve longer particle residence times (~3 seconds) and cooler temperatures in the zone just prior to the fly ash collection probe while slagging conditions involve residence times of 1 to 2 seconds and much higher temperatures in the collection zone. The resultant ash was analyzed for chemistry and particle size using CCSEM, similar to the analysis of coal minerals. More details of the DTF assembly are given below in the section on laboratory-scale combustion testing (Task 2).

3.3.3 Stochastic Model Development and Results

ATRAN1 has been modified and improved. The program now incorporates a mass balancing algorithm to extend its use to lower-rank coals. Three coals were chosen for testing the program: Eagle Butte subbituminous, Kentucky #9 bituminous, and a blend of Kentucky #9 (30%) and Eagle Butte (70%). These three coals were characterized using CCSEM, and the results were used to run ATRAN1. Figure 1 through 6 show comparisons of the experimental and predicted results for fly ash mineral phase compositions and PSDs for each of the test coals. ATRAN1 predicted fly ash compositions fairly well (Figures 1, 3, and 5), although there are still problems with modeling the interactions of calcium and iron with silicates and aluminum. The predicted PSDs were reasonably accurate for each of the Eagle Butte and Kentucky #9 parent fly ashes (Figures 2 and 4), but were unsatisfactory for the blend ash (Figure 6). The problems with prediction of PSD probably stem from the inadequacy of current methods for quantifying submicron particulates, especially for cases involving Ca-rich subbituminous coal. Eventual refinement and acceptance of the SEM-IA technique for individual submicron particles, as described separately below, may allow actual phases of individual grains to be determined for use in future versions of ATRAN1.

3.3.4 Particle Size and Composition Distribution Expert System

The ASHPERT expert system for fly ash particle size and composition distribution (PSCD) modeling has been completed. A significant accomplishment is the restructuring and expansion of the ASHPERT database. At the time of writing this report, the database contains the proximate/ultimate, XRF chemical fractionation, and CCSEM analyses data for 45 samples. Another significant accomplishment is the incorporation of the rule-based particle mineral-type classification expert system "MINER" into ASHPERT. This has considerably enhanced the applicability of ASHPERT in other areas of combustion systems modeling and also has permitted numerous algorithmic simplifications. Lastly, "hooks" for modules to perform statistical analyses of the database have been added to ASHPERT. This facilitates the recognition of patterns and trends in the data and expedites the formulation and modifications of ASHPERT's rules. A direct result of these additions and modifications is a measurable increase in ASHPERT's expertise which is now able to approximate PSCDs with an average error of 10% relative to their experimentally measured values.

Figure 1. Experimental and predicted compositions for Eagle Butte fly ash.

Figure 2. Experimental and predicted particle-size distributions for Eagle Butte fly ash.

Figure 3. Experimental and predicted compositions for Kentucky #9 fly ash.

Figure 4. Experimental and predicted particle-size distributions for Kentucky #9 fly ash.

Figure 5. Experimental and predicted compositions for Eagle Butte/Kentucky #9 blend fly ash.

Figure 6. Experimental and predicted particle-size distributions for Kentucky #9 blend fly ash.

The organization of this section is as follows. In Section 3.3.4.1 we discuss the PSCD modeling problem and the need for an empirical tool such as ASHPERT. A detailed description of the ASHPERT database is undertaken in Section 3.3.4.2. The ASHPERT knowledge base, its implementation, and the results obtained are described in Section 3.3.4.3. Section 3.3.4.4 contains remarks on future directions and extensions to ASHPERT.

3.3.4.1 Introduction

Particle size is fundamentally important in the combustion of pulverized coal and coal-water slurry. Ignition, stability, combustion efficiency, and pollutant formation are all strongly influenced by the fuel PSD. In addition, the compositions of individual particles play a major role in determining the chemical, thermal, and structural characteristics of ash deposits that accumulate on boiler walls and heat-transfer surfaces during combustion.

The evolutions of the PSCD functions are determined by a complex sequence of both cooperative and competing physical and chemical processes. Construction of a model to describe PSCD evolution is further complicated by the fact that PSCDs are, in general, dependent on the location within the boiler, and this location dependence is itself dependent on previous deposition histories. Thus, to solve the problem in any generality, a large set of coupled, ordinary and partial differential equations needs to be addressed. This set minimally includes the following:

- Navier-Stokes and continuity equations
- Species (kinetic) rate equations
- Species mass balance equations
- Heat equation with, in general, nonlinear, nonisotropic conductivity tensor, and nonlinear source terms
- Constitutive or other intra- and interparticle stress energy (tensor) relations

These equations, together with the complicated boundary conditions on boiler walls and heat-transfer surfaces, make the task of a general solution a formidable one.

The PSD models currently reported in the literature make certain simplifying assumptions regarding evolutionary mechanisms and may be categorized into two broad classes, viz., deterministic and stochastic. In deterministic models, the underlying principle is simply mass balance: a distribution $\phi(t)$ at time t is allowed to evolve to a distribution $\phi'(t')$ at time t' subject to the constraints that all process involved in transforming to preserve the net mass of the particles. All deterministic PSD models, therefore, can be succinctly described by an evolution equation of the form (4-7):

$$\frac{\delta\phi}{\delta t} = F(\phi)$$

The specific functional form of $F(\phi)$ above depends on the details of the processes (agglomeration, fragmentation, continuous or discrete mass loss, etc.) considered in the model.

In the case of stochastic approaches to PSD evolutions, the underlying idea is simply a redistribution of the initial distribution, but subject to some extremization principle or, failing that, subject to a set of empirically determined "local redistribution rules" (8-10). The stochastic models are thus computational or numerical in nature and are typified by Monte-Carlo or percolation lattice type calculations. In general, stochastic models, especially when ensemble-averaged, produce better results than their deterministic counterparts.

A major drawback of either the stochastic or the deterministic class of models is the difficulty in incorporating the (element or species) composition distributions and redistributions within their framework. Although it is conceptually very natural to speak of the species distributions giving rise to the particle's molar volume and, hence, its "size," computationally it is easier to deal with just a single distribution. However, composition distributions are indispensable in other combustion systems modeling areas such as fly ash deposition, NO_x, precipitator, and emissions control models.

Another drawback in regard to these deterministic and stochastic models is the difficulty of incorporating temperature as a parametric variable. The problem here is not so much as including temperature as a formal parameter of the model, but in the determination of the temperature dependence of the model-specific parameters (fragmentation rates, power law exponents, lattice bond breakage rates, etc). Lacking such data, the applicability of these models to PSD evolutions in situations involving sharp thermal gradients is limited. Although this limitation is indirectly redressed through randomizing the lattice bond breakage rates in the percolation lattice model (9), the assignment of probability measures to the lattice bond breakage events as a function of a (time-dependent) temperature distribution, which is physically appealing, does not appear to be straightforward.

The development of an expert system for approximating PSCD evolutions was undertaken primarily due to the widespread availability and growing acceptance of CCSEM analyses. CCSEM, which combines SEM, automated image analysis, and energy-dispersive x-ray spectroscopy, enables the analysis of a statistically significant number of particles and provides realistic representations of PSCDs both in the parent coal and its subsequent fly ash.

From a more pragmatic perspective, the compelling reason for an expert system is that it can serve as an interim tool for a "quick and dirty" means of providing realistic PSCDs to other areas of modeling while the refinement of the more rigorous and conventional approaches is in progress. In fact, conventional approaches too can benefit from the expertise of the system by defining additional goals and eliciting specific responses or even, in some circumstances, obtaining limits on model-specific parameters.

3.3.4.2 ASHPERT Database

The ASHPERT database is a relational database (11). The fundamental or basic tuple is a "sample" which is used as the generic term for a specimen of coal. (Note that the term sample is used in its statistical sense.) The attributes of each sample include a (unique) name, biography, location, rank, ownership category, proximate/ultimate, XRF, chemical fractionation, and CCSEM analyses. A sample need not have all its attributes included, i.e., values for some or all the attributes of a sample may be missing which facilitates

incremental updates of the database. The name field of the attribute of a sample, however, must be included since it serves as the primary (identification) key. A fairly sophisticated and general purpose database manager--which is itself a rule-based quasi-expert system--handles the routine chores of searching, sorting, indexing, report generation, and so on.

While many of the attributes of a sample are self-explanatory, a few comments are in order. The "name" attribute as mentioned earlier, is a mandatory field and should preferably be unique. The "biography" field permits biographical or other notes about the sample to become part of its record. Since some of the samples in the database have contractual or copyright restrictions regarding their data, the "ownership category" attribute of a sample serves to limit access to the sample data. Currently, only two ownership categories are supported, viz., PUBLIC and PRIVATE. A PUBLIC ownership category--the default--means that the sample does not have any access restrictions. A PRIVATE ownership category implies that the sample can be accessed only by the project manager or principal investigator of the project under which the sample was submitted for analysis. The project manager or principal investigator may authorize others access to PRIVATELY owned samples. The proximate attribute is another tuple with attributes moisture, volatile matter, fixed carbon, and ash. (This is the standard ASTM definition of a proximate analysis.) Likewise, the ultimate and XRF attributes correspond to the standard ASTM definition of ultimate and ash analyses. The default units for the attributes of the proximate, ultimate and XRF analyses fields is "weight percent," while the default analysis environment for the proximate and ultimate fields is "as-received." (These defaults can be changed.)

The CCSEM attribute is a more complex one. It is also a tuple with the attributes type, source, magnification, and file name. The "type" attribute which can be either COAL or ASH serves to distinguish the CCSEM analyses for the parent coal from its fly ash. The "source" field whose domain is DTF (drop-tube furnace), PPF (pilot-plant furnace), FSF (full-scale furnace), AFU (ash-fouling unit) or MINE (coal mine) can be used to identify the source of the coal or fly ash. Two "magnification" values are currently supported, viz., 50x and 240x, corresponding to the magnifications used in a CCSEM analysis. (A third magnification, 1000x, has recently been added to the CCSEM procedure and is soon expected to be supported.) The results of a CCSEM analysis are usually written to a file: the "file name" attribute thus is a placeholder for this information.

CCSEM analysis files contain the chemical and physical or geometric parameters for the particles in the analyzed sample (Coal/Ash). The format of these files are all identical: these are pure ASCII files, each line of which is the analysis data of a single particle. The files include columns for particle number, x-ray counts, normalized spectral intensities for the twelve elements analyzed, particle coordinates, particle diameter, area, perimeter, and shape factor. A detailed explanation of SEM analysis can be found in Goldstein and others (12) while that of CCSEM can be found in Dinger (13).

The entire ASHPERT database comprises data for 45 samples spread over 180 files and requires about 15MB of storage. As mentioned above, many of the samples are PRIVATELY owned, and thus the full database itself is expected to be distributed only to a restricted number of people. However, a version of ASHPERT will be available to the general public which will have a smaller

number of coals in the database. It is also expected that the database will increase in the near future; data for another 10 samples is almost complete. The compilation, entry, validation, and debugging of the database took about 14 months, with the majority of the time being spent in compilation and data entry. Approximately six months were spent in designing and developing the database manager and its associated set of software tools.

The 45 samples currently in the database represent widely variant ones in terms of geographic origin, bulk chemistry, rank, and combustion characteristics, as shown in Table 1.

A comparison of PSDs is also corroborative of the dispersed nature of this set of samples. However, some surprising trends are also to be observed. Figures 7 and 8 are the PSDs and MFDs (mineral frequency distributions) respectively, for a randomly selected set of six samples from the database. In order to respect the PRIVATE nature of some of the samples, the samples in the database have been serialized; the numbers appearing in Figures 7 and 8 are these serial numbers. A very striking trend immediately obvious from Figure 7 is the similarity in the "shape" of the PSD curve for the various coals and the corresponding fly ashes. All of these curves are similar to normal distribution curves with a "skewed" peak. This trend is not surprising because PSDs are expected to be "log-normal" distributions (14). A more unusual trend is the close tracking of the coal PSD curve by the fly ash PSD curve.

However, this "tracking" between the coal and fly ash PSD curves is not all too spectacular, as Figures 9 and 10 show. Figure 9, a scatter plot of the coal versus ash mean particle radii for the samples in the database, clearly exhibits the deviations between the coal and ash particle sizes. The solid regression line in this figure has an R^2 of only 0.07 and is a power law function of the form $y = ax^b$. Figure 10 is a scatter plot of the coal versus ash PSD curve standard deviations. Here, the points appear to be more tightly clustered, yet there are more outliers as well. The regression line is again a power law function with an R^2 of also about 0.07.

Figure 8 shows that no observable trend appears in the mineral distributions between the various coals. The numbers on the x-axis of the histograms are the mineral types. For example, mineral type 1 is quartz, mineral type 2 is alumina, etc. Likewise, there is no observable trend in the mineral distributions between the various fly ashes. However, the fly ash MFD appears to track the parent coal MFD fairly well, except for some of the major mineral types such as 1 (quartz), 9 (kaolinite), 11 (K-Al silicate), 13 (Ca-Al silicate), 20 (pyrite), and 33 (amorphous). Since the amorphous "mineral type" is a default mineral type, variations in the other mineral types will usually involve variations in the amorphous category.

Only a few coal-fly ash pair MFD curves have been displayed in Figure 8; thus one important trend that appears on viewing the MFDs for all the samples in the database is not easily observable. This trend relates to the continuity of the fly ash MFD on the parent coal's MFD: for instance, in Figure 8, the MFDs for coals 26 and 37 are fairly similar to each other; on comparing the MFD for ashes 26 and 37, it is seen that these are also similar and, what is more, the extent of the differences between the MFD for ashes 26 and 37 appears to be proportional to the extent of the differences between the MFD for these coals. The coal-fly ash pair MFD curves of the full database do

TABLE 1
ASHPERT Coal and Fly Ash Database

Coal Name	Rank	Location	Source of Fly Ash	% Ash
70% Eagle Bt/30% KY #9	Subbtuminous/Bituminous	WY/KY	DTF	7.3
75% Eagle Bt/25% KY #9	Subbtuminous/Bituminous	WY/KY	DTF	7.7
70% WY/30% OK Blend	Subbtuminous/Bituminous	WY/OK	Pilot	8.9
70% WY/30% OK Cleaned	Subbtuminous/Bituminous	WY/OK	Pilot	6.5
90% WY/10% OK Blend	Subbtuminous/Bituminous	WY/OK	Pilot	7.1
Beulah	Lignite	North Dakota	DTF	10.4
Bituminous	Bituminous	West Virginia	DTF	NA
Bituminous-High Load	Bituminous	Utah Han. Bas.	Full Scale	6.2
Bituminous-Low Load	Bituminous	Utah Han. Bas.	Full Scale	6.2
Dietz	Subbituminous	Montana PRB	DTF	4.6
Eagle Butte	Subbituminous	Wyoming PRB	DTF	5.6
Eagle Butte	Subbituminous	Wyoming PRB	Penn State Pilot	5.4
Eagle Butte	Subbituminous	Wyoming PRB	Full Scale	5.2
Illinois #6	Bituminous	Illinois	DTF	16.6
Illinois #6 MFP	Bituminous	Illinois	Pilot	4.2
Illinois #6 Parent	Bituminous	Illinois	Pilot	9
Illinois #6 SOAP	Bituminous	Illinois	Pilot	4.3
Island Creek	Bituminous	Kentucky	Pilot	6.8
Island Creek	Bituminous	Kentucky	Pilot-XS Air	6.7
Jader	Bituminous	Pennsylvania	Pilot-XS Air	8.7
Jader	Bituminous	Pennsylvania	Pilot	8.7
Kentucky #9	Bituminous	Kentucky	DTF	14.2
KY #9 Gravimelt 7a	Bituminous	Kentucky	DTF	0.5
Bituminous/Coke Blend	Lignite	Saskatchewan	Pilot	7.0
Bituminous	Bituminous	Mexico	Pilot	38.5
Subbituminous	Subbituminous/Bituminous	Wyoming	Pilot	3.6
Pitts #8 Gravimelt 9c	Bituminous	Pennsylvania	DTF	0.3
Pittsburgh #8 MFP	Bituminous	Pennsylvania	Pilot	3.3
Pittsburgh #8 Parent	Bituminous	Pennsylvania	Pilot	9.5
Pittsburgh #8 SOAP	Bituminous	Pennsylvania	Pilot	4.4
Robinson	Subbituminous	Montana	Penn State Pilot	8.6
Bituminous	Bituminous	Mexico	Pilot	30.1
San Miguel	Lignite	Texas	DTF	46.4
Subbituminous	Subbituminous/Bituminous	Philippines	Pilot	19.8
Subbituminous	Subbituminous	Wyoming PRB	Full Scale	4.89
Subbituminous	Subbituminous	Wyoming PRB	Full Scale	5.65
Subbituminous	Subbituminous	Wyoming PRB	Full Scale	4.94
Subbituminous	Subbituminous	Wyoming PRB	Full Scale	5.15
Subbit./Bit. Blend	Subbituminous/Bituminous	Wyoming PRB	Pilot	NA
Upper Freeport	Bituminous	Indiana	DTF	24.2
Upper Freeport MFP	Bituminous	Indiana	Pilot	5.4
Upper Freeport Parent	Bituminous	Indiana	Pilot	10.7
Upper Freeport SOAP	Bituminous	Indiana	Pilot	5.2
Utah Blind Canyon	Subbituminous	Utah Han. Bas.	DTF	6.1
Wyoming 100% (Wyodak)	Subbituminous	Wyoming	Pilot	8.0

Figure 7a. Particle-size distribution for Sample #5 from the ASHPERT database.

Figure 7b. Particle-size distribution for Sample #11 from the ASHPERT database.

Figure 7c. Particle-size distribution for Sample #14 from the ASHPERT database.

Figure 7d. Particle-size distribution for Sample #26 from the ASHPERT database.

Figure 7e. Particle-size distribution for Sample #37 from the ASHPERT database.

Figure 7f. Particle-size distribution for Sample #42 from the ASHPERT database.

(a) ASHPERT Samples #5, 11, and 14

(b) ASHPERT Samples #26, 37, and 42

Figure 8. Mineral frequency distribution for six samples from the ASHPERT database.

Figure 9. Mean particle radii for coals and corresponding fly ashes.

Figure 10. Standard deviations of the particle-size diameter curves for coals and ashes.

exhibit this trend, although there are instances where violations to this trend or "rule" are also observed. Since the continuity of the fly ash PSCD on the coal PSCD is one of the basic rules of ASHPERT (see next section), a more sophisticated analysis of the database to justify this rule will be one of the first tasks to be undertaken in related future work.

3.3.4.3 Implementation of ASHPERT

ASHPERT has been implemented as a loosely knit collection of support programs centered around a supervisory or control program (which is ASHPERT per se). The support programs include the relational database manager module(s), a library of database information specific to the ASHPERT database, postprocessing and data management procedures for proximate, ultimate, XRF, chemical fractionation, and CCSEM analysis data, a set of the more common statistical analysis routines, a dynamic library of inferential rules or methods, and a general purpose inference engine (which can "reason" both by backward and forward chaining). (It must also be noted that since ASHPERT's rules or methods may be complete programs in themselves, ASHPERT may also invoke operating system routines, and other application programs like compilers, linkers, etc.). A broad design philosophy such as this was deemed necessary if ASHPERT was to serve as a useful research tool and be able to evolve in step with its expanding knowledge base and expertise. The experience gained so far from working with ASHPERT has more than amply justified such a design philosophy. For instance, it took less than a week to modify, debug, and link the database routines to manage the restructured and expanded database. A drawback of such an approach, however, is that the program is not user friendly at all: a considerable amount of technical expertise and familiarity with the ASHPERT family of programs is expected of the user.

The dynamic knowledge base or inferential library facility of ASHPERT is especially useful in understanding, correlating, and extracting patterns in the data. Goals can be set on the fly, depending perhaps on the results of previous goals. Parameters can be altered dynamically and extensive simulations and "what-if" scenarios executed. For example, the MFD of a coal can be transformed to a hypothetical fly ash MFD depending on user-specified rules on how the transformation is to be performed. Such "rules," as mentioned earlier, may be entire procedures or programs (in C⁺⁺): ASHPERT will simply compile, link, and execute these programs. As another example, one may ask for all possible ways of transforming a coal MFD to its fly ash MFD. A useful result of such simulations, which are very time-consuming, is an understanding of the relative importance of the various modes--coalescence, fragmentation, surface recession, etc.--of transformation. Additionally, the results of such "data reduction" and exploratory goals can be appended to its knowledge base, adding to the expertise of the system.

One of the design goals of ASHPERT was, of course, an "expert" for predicting fly ash PSCDs from the parent coal's PSCD. This particular goal is thus an intrinsic or inbuilt goal in ASHPERT and can be invoked or "sought" whenever desired. Since the basic or primary assumption in PSCD evolutionary models is that identical coals, combusted under identical conditions, will behave identically, the key issue in formulating a set of rules for this goal is "when can a coal be considered not identical to another?" Rephrasing this question as "when is a coal a 'neighbor' or 'is in the neighborhood' of another coal?" it becomes clear that what is needed as "rules" is a

specification of a topology on the set C of all coals. Such a topology must reflect the intrinsic granularity or particulate nature of coals as well as their redistributions upon being transformed into fly ash. To this end, quite a few topologies have been implemented and tested. The PSD, EDF, and PSCD topologies described and tested in Ramanathan (15) were somewhat disappointing, with the predicted values in error by as much as 22.5%. A retest of these topologies with the expanded database did reduce the error, but only down to about 18%. An intense and fairly exhaustive statistical analysis of the database revealed surprisingly strong correlations between the coal MARS and fly ash MARS, where MARS (Mineral And (mean) Radius Space) is defined to be the subset:

$$\text{MARS} = \left\{ (m_1, \dots, m_p, \mu, \sigma) \mid \begin{array}{l} m_1 \geq 0, \dots, m_p \geq 0, m_1 + m_2 + \dots + m_p = 1 \\ \mu = \text{Mean (PSD)}, \sigma = \text{Std. Dev. (PSD)} \end{array} \right.$$

The MARS subset is thus seen to be the Cartesian product of the MFD vector with the PSD vector, with the latter being characterized by its mean radius and standard deviation. The simplest transformation model relating the coal MARS with the fly ash MARS subsets is, of course, the linear (or, more precisely the affine) transformation model. That is, we hypothesize that there exists a linear (affine) (and, hence, continuous) operator

$$T: \text{MARS}(\text{Coals}) \longrightarrow \text{MARS}(\text{Ash})$$

mapping coals to their corresponding fly ashes. In order to determine the operator T, an overdetermined system of linear equations with multiple right hand sides needs to be solved. An l_2 - norm minimizing solution has been obtained. Figures 11 and 12 show the experimental versus predicted scatter plots for the fly ash PSD mean radius and standard deviation, respectively. There is very little scatter in the plots: the experimental and predicted values agree very well, with an average error of about 5%. Parts (a-d) of Figure 12 show the experimental versus predicted fly ash mineral (relative) frequencies for the mineral types 1 (quartz), 9 (kaolinite), 20 (pyrite), and 33 (amorphous), respectively. Once again, very little scatter appears, and the largest average error is only about 8%. This MARS topology, together with the linear transformation model, is clearly seen to be the best of all the topologies and transformation models tested so far.

3.3.4.4 Prediction of Composition and Size for Unknown Coal

The predictive capabilities of ASHPERT were tested using the subbituminous Dietz coal from the Powder River Basin in Montana. Its composition, as determined using standard bulk and CCSEM analysis, is shown in Table 2. Ash was produced in the EERC DTF. Composition and size distributions of the drop-tube ash, as measured using CCSEM, was compared with the same data produced by ASHPERT. Figure 13 illustrates the experimental and predicted CCSEM phase compositions for the Dietz ash, on a frequency basis. The 33 phases identified using CCSEM (and also predicted with ASHPERT) are presented along the horizontal axis. There is a strong correlation between the measured and predicted phases in the Dietz fly ash. Major correlated phases include quartz (type 1), kaolinite (type 9), Ca-Al silicate (type 13), Ca aluminate (type 19), and the unknown/mixed category (type 33). Figure 14 shows the experimental and predicted size distribution frequencies. The size

(a) Mean radii

(b) Standard deviations

Figure 11. Experimental and predicted fly ash particle-size distributions.

Figure 12a. Experimental and predicted particle-size distribution for quartz.

Figure 12b. Experimental and predicted particle-size distribution for kaolinite.

Figure 12c. Experimental and predicted particle-size distribution for pyrite.

Figure 12d. Experimental and predicted particle-size distributions for "amorphous" type.

TABLE 2

Composition of Dietz Subbituminous Coal	
Parameter	Wt%
Proximate	
Moisture	23.66
Volatiles	31.95
Carbon	40.31
Ash	4.08
Ultimate	
Hydrogen	3.78
Carbon	54.91
Nitrogen	0.68
Sulfur	0.38
Oxygen	12.47
Ash	4.08
Oxides	
SiO ₂	36.0
Al ₂ O ₃	20.8
Fe ₂ O ₃	4.9
TiO ₂	2.2
P ₂ O ₅	0.7
CaO	13.3
MgO	4.5
Na ₂ O	2.2
K ₂ O	0.3
SO ₃	14.9
Minerals	
Quartz	30.8
Kaolinite	35.4
Montmorillonite	5.9
Aluminosilicate	2.1
Pyrite	11.7
Unknown	5.6
Total Minerals	3.2

distributions do not correlate as well as the phase composition data. The size distribution predicted by ASHPERT is skewed toward large particle sizes, suggesting the Dietz coal contains fine particulates (including organically associated material) which was not sufficiently described in the ASHPERT database. This problem will be mitigated by expansion and improvement of the database.

3.3.4.5 Conclusions

The ASHPERT expert system with a database of 45 coals and ashes has been tested using four different topologies and two different transformation models. The MARS topology with the linear transformation model appears to be the best rule combination, with an average error of 8%. The diversity of the ASHPERT database enables the program to be used in modeling a wide range of combustion systems.

Figure 13. Experimental and predicted CCSEM phase composition for Dietz coal ash, on a frequency basis.

Figure 14. Experimental and predicted particle-size distribution for Dietz coal ash, on a frequency basis.

4.0 TASK 2: LABORATORY-SCALE COMBUSTION TESTING

4.1 Introduction

Coals contain a variety of inorganic species including significant quantities of both organically associated cations and discrete minerals. Problems associated with inorganic constituents in coal combustion systems include ash deposition, formation of fine particulates, and corrosion and erosion of boiler parts. Of specific interest are the interactions between those inorganic constituents that result in the formation of low melting point phases during combustion and gas cooling. These phases are often the cause of ash deposition problems on boiler heat-transfer surfaces. The formation of low melting point phases results from complex physical and chemical transformations of inorganic components of coals during combustion. The transformations of the inorganic constituents depend upon their association in the coal and upon combustion conditions. Volatilization and condensation of sodium is being investigated using DTF experiments in order to gain insight into the formation of liquid phases in and on the surfaces of entrained ash particles. The primary goal of this task is to determine the factors affecting the size and composition of fly ash particles.

4.2 Equipment and Procedures

4.2.1 Drop-Tube Furnace System

The DTF is a laboratory-scale, entrained flow, tube furnace used to combust coal and produce ash under closely controlled conditions. Combustion parameters such as initial hot zone temperature, residence time, and gas cooling rate can be closely controlled and monitored.

The furnace system, shown in Figure 15, is housed in a three-floor laboratory specifically designed for safe and efficient operation of the system. The furnaces are mounted on guide rails extending through all three levels and can be moved to accommodate specific applications. The adjoining control room provides a clean, climate-controlled environment for the electronic equipment associated with the drop-tube system.

The furnace assembly consists of a series of vertical tube furnaces illustrated in Figure 16. These furnaces possess a total of four independently controlled, electrically heated zones. Each of these furnaces can be used separately or in conjunction with the others. This allows for maximum flexibility and precise control over combustion conditions.

Coal and primary and secondary air are introduced into the furnace system by means of a preheat injector. This system injects primary air and coal into the furnace at ambient temperature from a water-cooled probe assembly at the center of the tube. Secondary air is typically heated to 1000°C and introduced into the furnace through a mullite flow straightener. Thus the material to be combusted is introduced into the top of the furnace, along with preheated secondary air, and travels down the length of the furnace in a laminar flow regime. Various sampling probes or collection devices can be used with the DTF to collect ash samples. Downstream of the sampling probe and collection filter, the combustion gas is cooled and passes through a filter before entering a diaphragm pump. The pump is designed so that no air can leak into the sampling gas. The gas leaving the positive pressure side of

Figure 15. Drop-tube furnace facility.

Figure 16. Cross-sectional diagram of the drop-tube furnace.

the pump is passed through a flowmeter, which measures the volume of gas being pulled through the probe. After the flowmeter, part of the gas is directed through carbon monoxide, carbon dioxide, and oxygen analyzers. The concentrations of these gases can be read directly from the digital displays on the analyzers. The analog output signals from the analyzers are routed both to a chart recorder and to an A to D board on a personal computer (PC). The gas concentrations and the coal feed rates obtained from the coal feed system are logged by the PC for data interpretation. The configuration of this system is shown in Figure 17.

The coal feed system is designed to feed particles of various sizes in the pulverized coal range at rates of 0.05 to 0.5 g per minute and at primary carrier gas rates of approximately one liter per minute. The basic apparatus, shown in Figure 18, consists of a pressurized cylinder into which a container filled with coal is placed. A rotating brush and stirrer attached to a variable-speed motor feeds the coal from the container into a funnel where it is transported through the feed tubing into the furnace injector by the carrier gas. The coal feeder is mounted on a Mettler PM 2000 top-loading balance that is accurate to 0.01 gram. It is equipped with a RS232C interface which allows real-time coal feed rates to be read and stored on a PC.

A short residence time probe is used to collect ash samples at any residence length. The probe consists of four concentric, water-cooled, steel tubes. The outer shell is used to introduce the quench gas at the top of the probe. The combustion products pass through the innermost shell, and the remaining shells carry the cooling water. The probe is covered with an alumina insulating cylinder with an outer diameter of two inches (Figure 19).

The probe is inserted into the bottom of the furnace at a set distance calculated from the desired residence time. The quench gas and the vacuum are turned on. The coal is fed through the preheat injector, the combustion products are quenched upon entering the probe, and the residue char or ash is collected on a filter attached to the probe's innermost shell.

A fly ash quenching probe, shown in Figure 20, can be attached to the bottom of the DTF to cool the fly ash before collection. The system is reliable and versatile. Several collection devices can be added to the probe to collect fly ash.

The Environmental Protection Agency Southern Research Institute six-stage cyclone (EPAFSC) is used routinely to collect fly ash (Figure 21). The EPAFSC is designed to make six equally spaced particle-size cuts (d_{50}) on a logarithmic scale within the range of 0.1- to 10-millimeters diameter. The advantage of this system is that it can be used to collect the relatively large amounts of sample needed for chemical and morphological analysis.

In addition to the EPAFSC, the University of Washington Mark 5 source test cascade impactor (STCI) is used during selected combustion tests. The STCI was developed as a means of measuring the size distribution of particles in stacks and ducts at air pollution emission sources. The Mark 5 impactor produces size cuts of fly ash particles by inertial separation. These data are used for comparison with the EPAFSC data to provide more detailed information concerning the effects of combustion conditions on the size distribution of the fly ashes.

Figure 17. Configuration for sampling.

Figure 20. Fly ash quenching probe.

Figure 21. Six-stage multicyclone.

4.2.2 Determination of Carbon Conversion

The thermogravimetric analysis (TGA) determination of carbon conversion by the ash tracer method is performed on a small (approximately 50 mg) sample of the collected char giving information similar to that of a proximate analysis. The sample is heated in an argon atmosphere from ambient temperature up to 900°C. Weight loss from the sample between ambient and 110°C and from 110° to 900°C are reported as "moisture" and "volatile matter," respectively. Air is then introduced to combust the sample, and the resulting weight loss reported as "combustibles." The weight of the remaining residue is reported as "ash."

The use of bulk ash as a tracer to determine carbon loss is based on the assumption that there is no significant volatilization or loss of ash during TGA. From a similar TGA or proximate analysis of the parent coal, the percentage of ash in the parent coal has also been determined. It is assumed that the amount of ash has not changed; hence the increase in percentage of ash in the collected char is a measure of the carbon consumed during combustion and calculated by:

$$\% \text{ carbon converted} = 100 \left[1 - \frac{OA}{RA} \frac{RV+RC}{OV+OC} \right] \quad [\text{Eq. 1}]$$

where OA = % ash in the original coal
 RA = % ash in the residue collected
 OV = % volatile matter in the original coal
 RV = % volatile matter in the residue collected
 OC = % combustibles in the original coal
 RC = % combustibles in the residue collected

The determination of carbon conversion by TGA using the ash tracer method tends to be relatively inaccurate due to 1) the small quantities of sample used, 2) the assumption that no ash is lost from the sample before analysis, and 3) the insensitivity of the method during the early stage of combustion (0%-25% conversion).

Calculation of carbon conversion by the gas analysis method uses the gas flow rate and the ideal gas law, $PV = nRT$, to convert the concentrations of CO_2 and CO in the gas stream into molar quantities. The molar feed rate of carbon was calculated from the coal feed rate and the percentage of carbon in the ultimate analysis of the fuel. The equations for the calculation are as follows:

$$\text{moles } \text{CO}_2 = (\text{total gas flow rate}) \frac{\frac{\% \text{CO}_2}{100} \frac{P}{760 \text{ mm Hg}}}{R \cdot T_k} \quad [\text{Eq. 2}]$$

$$\text{moles } \text{CO} = (\text{total gas flow rate}) \frac{\frac{\% \text{CO}}{100} \frac{P}{760 \text{ mm Hg}}}{R \cdot T_k} \quad [\text{Eq. 3}]$$

where P is the barometric pressure (mm Hg), R is the universal gas constant (0.082 L atm/mole K), and T_k is the gas temperature in Kelvin. The carbon feed rate is calculated by:

$$\text{molar feed rate} = \frac{\% \text{ carbon}}{100} (\text{coal feed rate}) \frac{1 \text{ mole}^\circ\text{C}}{12 \text{ g}^\circ\text{C}} \quad [\text{Eq. 4}]$$

and the percent carbon conversion is calculated by:

$$\% \text{ carbon conversion} = \frac{\text{moles } \text{CO}_2 + \text{moles } \text{CO}}{\text{molar feed rate}} 100\% \quad [\text{Eq. 5}]$$

Factors that can influence the determination of carbon conversion by gas analysis are 1) decreased gas analyzer sensitivity and a very steep calibration curve for the CO_2 analyzer at low concentrations, 2) accuracy of the coal feed rates, and 3) fluctuations in the vacuum flowmeter which determines how much gas is being sampled (the molar concentrations of CO and CO_2 are based on the liters per minute of gas passing through this flowmeter). This occasionally results in carbon conversion percentages that exceed 100%.

The amount of coal burned was calculated from the weight loss of the coal fed in the DTF. The amount of ash fed is determined from the percent ash in the coal, derived from a proximate analysis, multiplied by the amount of coal fed. The char or residue that is left from the test is collected on a filter and weighed. The percentage of carbon conversion is then calculated by:

$$\% \text{ carbon conversion} = 100 \frac{\text{char collected (g)} - \text{ash (g) fed}}{\text{coal fed (g)} - \text{ash fed (g)} - \text{water fed (g)}} \quad [\text{Eq. 6}]$$

The calculation of the percentage of coal burned using the weight loss method tends to be higher than that of the percentage of carbon loss determined by the gas analysis method due to the assumption that all of the ash and unburned coal is collected and weighed. In practice, some of the uncombusted material may not reach or be retained on the filter before weighing, resulting in higher conversion values than actually obtained.

4.3 Formulation of Synthetic Coals

4.3.1 Introduction

Synthetic coal model mixtures provide an excellent means of studying inorganic transformations in a physically and chemically controlled system because the complexity of inorganic reactions that occur in real coal systems is minimized. Accurate quantities and sizes of known minerals can be included in a synthetic organic matrix in order to isolate specific reactions and transformations of selected inorganic constituents. A controlled combustion environment, such as a DTF, is used to combust the model mixture. Key phenomena to be studied include fragmentation of the synthetic coal grains and coalescence of the inorganics within the synthetic coal particles.

The goal of the model mixture studies during this past year was to perform combustion testing on three model mixtures, including:

- Sodium-silica-sulfur system (simulation of organically bound Na).
- Calcium-silica-sulfur system (simulation of organically bound Ca).
- Calcium-silica-sulfur system (mineral-bound Ca as calcite).
- Iron-aluminosilicate system (using pyrite and kaolinite).

The purpose of using the Ca-Si-S systems was to demonstrate the differences in interactions between included quartz and 1) Ca that is mineral bound as included calcite, and 2) Ca that is organically bound or dispersed on an ionic level within the organic matrix. The reactions involving Ca, Si, and S during combustion are of particular interest when burning low-sulfur and calcium-rich western U.S. subbituminous coals, since calcium sulfate and calcium silicate phases play important roles in the formation of convective pass ash deposits. The effect of temperature on the particle size and composition distribution of ash produced from included calcite and quartz and organically associated calcium and quartz are of specific interest, as are the reactions of sulfur oxides with the available calcium oxide. Past work (3,16) on a Na(org.)-Si-S system has shown that higher temperatures result in the formation of smaller ash particles, probably due to the fragmentation of the chars. Additional work was conducted on the Na(org.)-Si-S system to add another dimension to the role of organically associated elements in the formation of ash, especially with regard to the formation of low melting point Na sulfates and Na silicates on the surface of quartz particles.

The purpose of studying the Fe-Al-Si system was to examine the interactions between pyrite and an alumina-silica clay. Such minerals have a significant effect on slag viscosity when firing eastern bituminous coals.

4.3.2 Methodology

Preparation of the synthetic coal is modified from Senior (17), as outlined by Erickson (18) and Ludlow and others (16). The procedure for preparing the synthetic coals has been described in detail previously for the organic Na-Si-S, organic Ca-Si-S, and calcite-Si-S synthetic coals (19). The preparation of the Fe-Si-Al synthetic coal is similar. Briefly, the synthetic coal is produced from the product of the polymerization of furfural alcohol in six steps: 1) polymerization of furfural alcohol using p-toluenesulfonic acid as a catalyst, 2) addition of carbon black and intrinsic mineral matter, 3) removal of acetone, 4) high-temperature curing of the polymer, 5) grinding and sizing of the cured polymer, and 6) addition of extrinsic matter.

Each of the synthetic mixtures was comprised of approximately 250 g of unsized coal which was then sonic-sieved to produce approximately 50-g samples of 38- to 106- μm synthetic coal. Since the mineral matter sizes are smaller than the selected coal size fraction, excluded minerals inadvertently produced by the grinding operation are removed by the sizing step.

Two calcium, silica, and sulfur synthetic coal systems were prepared: one system having calcium in the mineral form as 10- μm calcite (Ca[min.]-Si-S) and the other having calcium associated in a simulated organic association as ionically dispersed calcium acetate (Ca[org.]-Si-S). A third system consisted of sodium, silica, and sulfur, with the sodium being associated as sodium benzoate, simulating an organic association (Na[org.]-Si-S). Silica, in all three systems, consisted of 10- μm quartz that was associated within the synthetic coal particles. Sulfur was extraneously added to these model mixtures in an elemental form and was also included in the organic polymer in very small amounts. The calcite particles were added to the organic matrix during polymerization to allow for their incorporation into the synthetic coal particles.

The iron-aluminosilicate synthetic coal system was prepared with iron in the form of pyrite (FeS_2), of mean size 13.5 μm , and kaolinite ($\text{Al}_2[\text{Si}_2\text{O}_5][\text{OH}]_4$), of mean size approximately 5 μm , added as intrinsic mineral matter. Aside from the pyrite, a small amount of included sulfur results from the p-toluenesulfonic acid catalyst used. Carbon black equal to approximately 1/3 of the polymer weight was added intrinsically to the model mixtures.

The synthetic coals were combusted in the DTF using a one-furnace configuration. Runs were made for the model mixtures at four temperatures: 900°, 1100°, 1300°, and 1500°C. Varied particle residence time runs of 0.1, 0.2, and 0.8 seconds were performed at 900° and 1500°C on the Ca(org.)-Si-S, Ca(min.)-Si-S, and the Fe-Al-Si coal systems. The combustion ash and chars are being analyzed using CCSEM, Malvern, TGA, and XRD analyses. Carbon conversion rates were calculated for the chars.

Pure pyrite used in the production of the Fe-Al-Si model mixture was also injected into the DTF at 900° and 1500°C using air as the carrier gas and at 1500°C under a nitrogen atmosphere. The residues were collected on a bulk filter and submitted for analysis.

The fly ash collected on the bulk filters was analyzed to determine particle-size and composition distributions using CCSEM (20). Approximately

2000 ash particles were analyzed for each sample using CCSEM. The primary outputs of CCSEM are particle average diameters, particle aspect ratios or shape factors, and particle compositions expressed as normalized x-ray energy counts for twelve major elements. In addition, the x-ray counts are corrected and used to identify inorganic phases using stoichiometric constraints. This allows for comparisons of quantities of specific mineral phases between ash samples. In the case of fly ash, there are very few true minerals; however, particles may have compositions that are close to identifiable phases. The ash samples were prepared and analyzed in two different ways: 1) as whole grain mounts by dispersing them onto a filter which essentially gives a surface analysis of the particles (depth of electron beam penetration was between 1 and 2 μm), and 2) as cross-sectioned epoxy mounts which give an interior analysis of the particle. Malvern sizing, a laser-based particle-sizing technique, was also performed on each of the ash samples, and x-ray diffraction analysis was performed on selected ash samples to verify some of the CCSEM mineral determinations.

4.3.3 Results

4.3.3.1 Inorganic Composition of the Synthetic Coals

The projected quantity of inorganic components in the three synthetic coal model mixtures (on a synthetic coal basis) was compared to the actual levels obtained. The results are summarized as follows:

1. Ca(min.)-Si-S: CaO (5%), S (1%), and SiO₂ (10%), where the calcium was added as limestone during the polymerization along with the SiO₂ to inherently bind it. The sulfur was added extraneously after polymerization. Actual analysis on a synthetic coal basis was CaO (3.5%), S (1.1%), and SiO₂ (11.7%).
2. Ca(org.)-Si-S: CaO (5%), S (1%), and SiO₂ (10%), where the calcium is bound organically, the sulfur was added extraneously, and the SiO₂ was added to the coal during the polymerization to bind it inherently in the coal. The actual analysis on a synthetic coal basis was CaO (0.3%), S (0.6%), and SiO₂ (6.8%).
3. Na(org.)-Si-S: Na₂O (5%), S (1%), and SiO₂ (10%), where the sodium is bound organically by adding Na benzoate, the sulfur was added extraneously, and the SiO₂ was added to the coal during polymerization to inherently bind it in the coal. Actual analysis on a synthetic coal basis was Na₂O (1%), S (0.6%), and SiO₂ (8%).

Some of the sulfur was derived from the catalyst used in the polymerization of the synthetic coal. The sulfur was less than 1%, so additional sulfur was added extraneously to obtain a sulfur level of approximately 1% total. Some problems were encountered in formulating the desired inorganic constituent contents, especially for the mixtures containing organically associated sodium and calcium.

4.3.3.2 Results of the Combustion Tests of the Synthetic Coals

The Na(org.)-Si-S, Ca(org.)-Si-S, Ca(min.)-Si-S, and Fe(min.)-Al-Si synthetic coal systems were fired in the DTF at various temperatures and

residence times to calculate conversion rates. The combustion runs were made for each model mixture at four temperatures: 900°, 1100°, 1300°, and 1500°C. The initial oxygen concentration for testing was set at 21% for all tests. Ash samples were collected and gas analysis recorded during each test. Table 3 shows the run conditions for each test. For each system, at each temperature, ash was collected on a bulk filter at longer residence times of over two seconds. Carbon conversion was calculated from both gas and TGA analyses for these longer residence time runs. Carbon conversion was also determined from the loss of weight of the total amount of coal fed. Table 4 shows the proximate analyses results. Table 5 shows the comparison of carbon conversion calculated from the gas analysis, from TGA results, and from the weight loss method. Varied particle residence time runs of 0.1, 0.2, and 0.8 seconds were also performed at 900° and 1500°C on the Ca(org.)-Si-S, Ca(min.)-Si-S, and Fe(min.)-Al-S systems. Carbon conversion was determined for these tests (Table 5). Table 4 shows the TGA results. The combustion ash and chars were subsequently analyzed using CCSEM, Malvern, TGA, and XRD analyses.

Figure 22 shows the carbon conversion tests as determined by gas analysis at 900°C. Figure 23 shows the carbon conversion at 1500°C. The conversion of the Ca[org]-Si-S system with the organically bound calcium was significantly more rapid than that of the Ca(min.)-Si-S system with the mineral calcium at the lower temperature. About 50% carbon conversion of the Ca-Si-S system (mineral calcite) was not obtained until approximately 2.4 sec. At 1500°C, the organic Ca blend shows greater conversion at the 0.1-second residence time with the mineral Ca blend obtaining the same conversion as the organic Ca blend at approximately 0.5 seconds and thereafter. The Fe(min.)-Al-Si system exhibits essentially the same carbon conversion behavior as the Ca(min.)-Si-S system. The anomalously low conversion for the Fe(min.)-Al-Si material at 1500°C and 0.2-sec residence time is probably an experimental artifact.

The enhanced rate of conversion of the material with the organic calcium is in agreement with previous studies on the effect of organically bound calcium on demineralized lignite chars in which the organic calcium appeared to act as a catalyst to enhance the char-burning rate at lower temperatures (21).

An interesting result is the substantial negative conversions obtained for the Fe(min.)-Al-Si chars at 0.1- and 0.2-sec residence time from the TGA analysis method, as seen in Table 4. The percentage of volatile matter and fixed carbon in the 0.1- and 0.2-sec residence time chars is determined to be more than in the starting coal. A possible explanation is the decomposition of pyrite during TGA.

4.3.4 Mineral Transformations in the Synthetic Coals

Table 6 gives a summary of the composition of the Ca(min.)-Si-S synthetic coal ash and combustion ash products, including cross-section and surface CCSEM analyses and XRD crystalline phase identifications. The XRD analysis indicates that the calcite grains have transformed and reacted to produce Ca(OH)₂, CaO, anhydrite (CaSO₄), and amorphous calcium silicate. The Ca(OH)₂ may be a product of CaO reacting with the moisture in air. The amorphous calcium silicate appears to be more prevalent at higher temperatures and is abundant both in the interior and at the surface of the ash particles, possibly an indicator as to the extent of the reaction that has taken place.

TABLE 3

Run Conditions for DTF Synthetic Coal Tests

Test ID	Syn. Coal Type	Res. Time (sec)	DTF Temp. (°C)	O ₂ Init. (%)	Feed Rate (g/m)	CO ₂ Calc. (%)	CO Calc. (%)	O ₂ Calc. (%)	Pri. Flow (L/m)	Sec. Flow (L/m)	Quench Flow (L/m)	Vac. Flow (L/m)	CO ₂ Moles (min)	CO Moles (min)	Pb Press (mm Hg)	(Amb.) Temp. (°C)	Carbon Orig. (%)	Gas Carbon Conv. (%)
SYN-0391	Ca-Si-S (min.)	0.10	900	21.0	0.092	0.05	0.0368	21.16	0.8	3.2	3.0	7.0	0.0001	0.000059	748.77	24.5	80.34	2.36
SYN-0291	Ca-Si-S (min.)	0.20	900	21.0	0.102	0.10	0.0543	20.68	0.8	3.2	3.0	7.0	0.0002	0.000088	748.77	24.5	80.34	3.64
SYN-0191	Ca-Si-S (min.)	0.80	900	21.0	0.095	0.04	0.0221	20.84	0.8	3.2	3.0	7.0	0.0001	0.000036	748.77	24.5	80.34	1.54
SYN-2591	Ca-Si-S (min.)	0.80	900	21.0	0.107	0.19	0.0562	20.64	0.8	3.2	3.0	7.0	0.0003	0.000091	748.77	24.5	80.34	5.46
SYN-0491	Ca-Si-S (min.)	2.89	900	21.0	0.083	3.55	0.0037	17.88	0.8	3.2	3.0	7.0	0.0056	0.000006	732.17	25.5	80.34	100.66
SYN-0591	Ca-Si-S (min.)	2.68	1100	21.0	0.089	3.82	0.0000	17.39	0.8	3.2	3.0	7.0	0.0061	0.000000	734.48	23.5	80.34	101.86
SYN-0791	Ca-Si-S (min.)	2.47	1300	21.0	0.103	4.16	0.0001	17.23	0.8	3.2	3.0	7.0	0.0065	0.000000	730.34	26.0	80.34	94.55
SYN-1091	Ca-Si-S (min.)	0.10	1500	21.0	0.105	0.55	0.0735	20.19	0.8	3.2	3.0	7.0	0.0009	0.000114	728.73	28.0	80.34	13.87
SYN-0991	Ca-Si-S (min.)	0.20	1500	21.0	0.093	1.74	0.1663	19.37	0.8	3.2	3.0	7.0	0.0027	0.000258	728.73	28.0	80.34	47.68
SYN-0891	Ca-Si-S (min.)	0.80	1500	21.0	0.110	4.77	0.0070	16.60	0.8	3.2	3.0	7.0	0.0074	0.000011	728.73	28.0	80.34	100.70
SYN-0691	Ca-Si-S (min.)	2.28	1500	21.0	0.097	3.82	0.0000	17.58	0.8	3.2	3.0	7.0	0.0061	0.000000	736.06	25.0	80.34	93.19
SYN-2491	Ca-Si-S (org.)	0.10	900	21.0	0.100	0.37	0.1295	20.55	0.8	3.2	3.0	7.0	0.0006	0.000206	744.82	28.0	91.13	10.36
SYN-2391	Ca-Si-S (org.)	0.20	900	21.0	0.094	0.17	0.0744	20.70	0.8	3.2	3.0	7.0	0.0003	0.000118	744.82	28.0	91.13	5.52
SYN-2291	Ca-Si-S (org.)	0.80	900	21.0	0.096	3.49	0.1129	17.98	0.8	3.2	3.0	7.0	0.0055	0.000179	744.82	28.0	91.13	78.55
SYN-1391	Ca-Si-S (org.)	2.37	900	21.0	0.099	3.79	0.0018	21.00	0.8	3.2	3.0	7.0	0.0060	0.000003	738.49	26.0	91.13	79.93
SYN-1491	Ca-Si-S (org.)	2.27	1100	21.0	0.112	4.63	0.0000	17.01	0.8	3.2	3.0	7.0	0.0073	0.000000	738.28	27.0	91.13	86.06
SYN-1591	Ca-Si-S (org.)	2.15	1300	21.0	0.100	4.19	0.0000	17.53	0.8	3.2	3.0	7.0	0.0066	0.000000	737.97	28.0	91.13	87.11
SYN-2191	Ca-Si-S (org.)	0.10	1500	21.0	0.089	1.47	0.1085	19.64	0.8	3.2	3.0	7.0	0.0024	0.000174	745.74	25.0	91.13	37.58
SYN-2091	Ca-Si-S (org.)	0.20	1500	21.0	0.112	2.65	0.1418	18.72	0.8	3.2	3.0	7.0	0.0043	0.000228	745.74	25.0	91.13	52.78
SYN-1991	Ca-Si-S (org.)	0.80	1500	21.0	0.103	4.77	0.0026	16.59	0.8	3.2	3.0	7.0	0.0075	0.000004	744.74	29.0	91.13	96.48
SYN-1891	Ca-Si-S (org.)	2.03	1500	21.0	0.106	4.53	0.0000	16.93	0.8	3.2	3.0	7.0	0.0072	0.000000	741.56	26.0	91.13	89.88
SYN-1191	Na-Si-S	2.49	900	21.0	0.105	4.04	0.0018	17.30	0.8	3.2	3.0	7.0	0.0064	0.000003	731.60	26.0	85.04	85.40
SYN-1291	Na-Si-S	2.37	1100	21.0	0.105	4.10	0.0000	17.18	0.8	3.2	3.0	7.0	0.0064	0.000000	732.40	28.0	85.04	86.41
SYN-1691	Na-Si-S	2.23	1300	21.0	0.095	4.20	0.0000	17.50	0.8	3.2	3.0	7.0	0.0066	0.000000	737.97	28.0	85.04	98.21
SYN-1791	Na-Si-S	2.09	1500	21.0	0.108	4.60	0.0000	16.89	0.8	3.2	3.0	7.0	0.0072	0.000000	738.00	30.0	85.04	94.06
SYN-3191	Fe-Al-Si	0.10	900	21.0	0.102	0.01	0.0119	20.80	0.8	3.2	3.0	7.2	0.0000	0.000018	739.48	32.0	84.02	0.49
SYN-3091	Fe-Al-Si	0.20	900	21.0	0.100	0.01	0.0035	20.84	0.8	3.2	3.0	7.2	0.0000	0.000005	739.48	32.0	84.02	0.28
SYN-2991	Fe-Al-Si	0.80	900	21.0	0.100	0.01	0.0087	20.79	0.8	3.2	3.0	7.2	0.0000	0.000014	739.48	32.0	84.02	0.46
SYN-3291	Fe-Al-Si	3.55	900	21.0	0.101	4.39	0.0020	16.88	0.8	3.2	3.0	7.2	0.0068	0.000003	739.48	32.0	84.02	96.57
SYN-3391	Fe-Al-Si	3.15	1100	21.0	0.091	3.91	0.0009	17.42	0.8	3.2	3.0	7.2	0.0062	0.000002	741.88	26.0	84.02	97.69
SYN-3491	Fe-Al-Si	2.82	1300	21.0	0.098	4.18	0.0011	17.28	0.8	3.2	3.0	7.2	0.0067	0.000002	744.20	26.0	84.02	97.29
SYN-2891	Fe-Al-Si	0.10	1500	21.0	0.089	0.71	0.0511	20.06	0.8	3.2	3.0	7.2	0.0011	0.000081	739.90	27.0	84.02	19.28
SYN-2791	Fe-Al-Si	0.20	1500	21.0	0.095	0.45	0.0347	20.13	0.8	3.2	3.0	7.2	0.0007	0.000055	739.90	27.0	84.02	11.43
SYN-2691	Fe-Al-Si	0.80	1500	21.0	0.098	4.39	0.0040	16.70	0.8	3.2	3.0	7.2	0.0070	0.000006	739.90	27.0	84.02	101.42
SYN-3591	Fe-Al-Si	2.55	1500	21.0	0.101	4.38	0.0013	16.61	0.8	3.2	3.0	7.2	0.0070	0.000002	742.79	26.0	84.02	98.86

TABLE 4

TGA Results for Synthetic Coal Chars and Ashes

Run No.	Syn. Coal Sample	H ₂ O %	Vol%	Fixed Carbon %	Ash %
COAL	Ca-Si-S (min.)	0.59	5.04	76.04	18.34
COAL	Na-Si-S	2.60	13.74	74.30	9.35
COAL	Ca-Si-S (Org.)	1.00	8.37	82.93	7.68
COAL	Fe-Al-Si	1.00	7.52	80.69	10.77
CIT-SYN-0191	Ca-Si-S (min.)	0.74	4.70	77.92	16.64
CIT-SYN-0291	Ca-Si-S (min.)	0.78	5.66	72.98	20.58
CIT-SYN-0391	Ca-Si-S (min.)	0.72	3.90	73.58	21.82
CIT-SYN-0491	Ca-Si-S (min.)	0.04	0.90	-0.29	99.34
CIT-SYN-0591	Ca-Si-S (min.)	0.10	0.21	-0.33	100.00
CIT-SYN-0691	Ca-Si-S (min.)	0.08	0.01	-0.15	100.10
CIT-SYN-0791	Ca-Si-S (min.)	0.10	0.26	0.00	99.65
CIT-SYN-0891	Ca-Si-S (min.)	0.19	1.70	-0.31	98.41
CIT-SYN-0991	Ca-Si-S (min.)	0.70	4.53	64.92	29.83
CIT-SYN-1091	Ca-Si-S (min.)	0.92	6.69	66.88	25.53
CIT-SYN-1191	Na-Si-S	2.68	9.74	23.79	63.96
CIT-SYN-1291	Na-Si-S	2.53	4.58	0.17	92.70
CIT-SYN-1491	Ca-Si-S (org.)	0.00	0.27	1.29	98.50
CIT-SYN-2091	Ca-Si-S (org.)	3.54	1.48	83.46	11.55
CIT-SYN-2191	Ca-Si-S (org.)	4.01	2.01	83.52	10.47
CIT-SYN-2291	Ca-Si-S (org.)	1.49	1.70	78.30	18.49
CIT-SYN-2391	Ca-Si-S (org.)	6.08	3.52	81.52	8.90
CIT-SYN-2491	Ca-Si-S (org.)	6.21	2.79	82.08	8.90
CIT-SYN-2591	Ca-Si-S (min.)	4.42	7.01	68.25	20.33
CIT-SYN-2691	Fe-Al-Si	0.65	2.05	7.32	89.97
CIT-SYN-2791	Fe-Al-Si	2.12	4.57	84.23	9.07
CIT-SYN-2891	Fe-Al-Si	1.80	6.00	83.83	8.37
CIT-SYN-2991	Fe-Al-Si	0.85	6.41	82.17	10.66
CIT-SYN-3091	Fe-Al-Si	0.94	6.60	84.17	8.60
CIT-SYN-3191	Fe-Al-Si	0.68	6.48	82.79	10.06
CIT-SYN-3291	Fe-Al-Si	0.55	4.19	6.30	88.96
CIT-SYN-3391	Fe-Al-Si	0.32	0.77	0.09	98.85

TABLE 5

Carbon Conversion Results for Synthetic Coals

Test ID	Syn. Coal Type	Res. Time (sec)	Temp. (°C)	Ash-Fired (g)	Coal Fed (g)	Ash Fed (g)	Residue (g)	Coal Burned by wt% ^a	Gas Carbon Conv. (%) ^b	TGA Carbon Conv. (%) ^c
SYN-0391	Ca(min.)	0.10	900	5.42	2.72	0.49	2.63	4.13	2.36	19.70
SYN-0291	Ca(min.)	0.20	900	5.16	3.08	0.55	2.83	9.80	3.64	13.60
SYN-2591	Ca(min.)	0.80	900	5.01	1.60	0.29	1.43	13.08	5.46	16.30
SYN-0191 ^d	Ca(min.)	0.80	900	5.13	2.92	0.52	2.67	10.48	1.54	-12.30
SYN-0491	Ca(min.)	2.89	900	0.84	2.51	0.45	0.38	103.44	100.66	99.90
SYN-0591	Ca(min.)	2.68	1100	0.83	2.74	0.49	0.41	103.65	101.86	100.00
SYN-0791	Ca(min.)	2.47	1300	0.84	2.07	0.37	0.31	103.43	94.55	99.90
SYN-1091	Ca(min.)	0.10	1500	4.48	1.05	0.19	0.84	24.41	13.87	34.80
SYN-0991	Ca(min.)	0.20	1500	3.05	0.95	0.17	0.52	55.51	47.68	47.30
SYN-0891	Ca(min.)	0.80	1500	0.84	2.21	0.39	0.33	103.47	100.70	99.70
SYN-0691	Ca(min.)	2.28	1500	0.83	1.98	0.35	0.29	103.61	93.19	100.00
SYN-2491	Ca(org.)	0.10	900	11.23	1.00	0.08	0.86	14.86	10.36	19.80
SYN-2391	Ca(org.)	0.20	900	11.80	0.94	0.07	0.85	10.11	5.52	19.60
SYN-2291	Ca(org.)	0.80	900	3.62	2.41	0.19	0.67	78.24	78.55	63.60
SYN-1391	Ca(org.)	2.37	900	1.22	2.96	0.23	0.28	98.14	79.93	NA
SYN-1491	Ca(org.)	2.27	1100	0.91	3.33	0.26	0.23	100.74	86.06	99.90
SYN-1591	Ca(org.)	2.15	1300	0.91	3.04	0.23	0.21	100.73	87.11	NA
SYN-2191	Ca(org.)	0.10	1500	8.97	0.88	0.07	0.61	33.71	37.58	31.30
SYN-2091	Ca(org.)	0.20	1500	7.43	1.12	0.09	0.64	46.50	52.78	38.10
SYN-1991	Ca(org.)	0.80	1500	0.80	3.09	0.24	0.19	101.66	96.48	NA
SYN-1891	Ca(org.)	2.03	1500	0.86	3.15	0.24	0.21	101.13	89.88	100.00
SYN-1191	Na(org.)	2.49	900	1.22	3.16	0.30	0.36	97.71	85.40	94.40
SYN-1291	Na(org.)	2.37	1100	0.82	3.13	0.29	0.24	101.88	86.41	99.50
SYN-1691	Na(org.)	2.23	1300	0.72	2.85	0.27	0.19	102.86	98.21	NA
SYN-1791	Na(org.)	2.09	1500	0.66	3.25	0.30	0.20	103.46	94.06	NA
SYN-3191	Fe-Al-Si	0.10	900	8.43	2	0.17	1.40	10.25	0.49	-8.34
SYN-3091	Fe-Al-Si	0.20	900	8.75	2	0.16	1.43	6.42	0.28	-28.84
SYN-2991	Fe-Al-Si	0.80	900	8.39	3	0.32	2.72	10.80	0.46	-1.46
SYN-3291	Fe-Al-Si	3.55	900	0.96	3	0.33	0.32	100.48	96.57	98.56
SYN-3391	Fe-Al-Si	3.15	1100	0.83	3	0.30	0.25	101.99	97.69	99.89
SYN-3491	Fe-Al-Si	2.82	1300	0.80	3	0.32	0.25	102.39	97.29	NA
SYN-2891	Fe-Al-Si	0.10	1500	6.62	2	0.19	1.27	32.19	19.28	-31.06
SYN-2791	Fe-Al-Si	0.20	1500	6.73	2	0.21	1.39	30.80	11.43	-19.52
SYN-2691	Fe-Al-Si	0.80	1500	1.00	2.93	0.32	0.32	100.02	101.42	98.73
SYN-3591	Fe-Al-Si	2.55	1500	0.77	3	0.33	0.25	102.81	98.86	NA

^a Derived from original proximate analysis.^b Derived from ultimate analysis carbon %.^c Derived from residue TGA and original proximate analysis.^d Test repeated (SYN-2591).

Figure 22. Synthetic coal carbon conversion test results at 900°C.

Figure 23. Synthetic coal carbon conversion test results at 1500°C.

TABLE 6

Mineral and Amorphous Phase Composition of
Ca(min.)-Si-S Synthetic Coal and Fly Ash (wt%)

		Fly Ash			
Mineral/Phase	Syn. Coal	900°C	1100°C	1300°C	1500°C
CCSEM Cross-Section Analysis					
Quartz	54.0	42.6	52.7	52.9	48.1
Calcite/CaO	39.9	8.5	4.0	18.4	14.0
Ca Silicate	0.8	18.5	39.4	21.5	28.2
Gypsum/Anhydrite	0.1	0.9	0.2	0.0	0.0
Ca-Si-S Mixture	4.7	27.6	3.5	6.9	9.4
CCSEM Surface Analysis					
Quartz	--	42.0	41.1	32.7	43.1
Calcite/CaO	--	2.8	3.3	6.4	9.8
Ca Silicate	--	10.5	15.3	17.7	26.1
Gypsum/Anhydrite	--	12.9	7.2	19.1	0.0
Ca-Si-S Mixture	--	31.5	31.5	22.4	20.6
XRD Bulk Analysis					
Major	Quartz Calcite	Quartz	Quartz	Quartz	Quartz
Minor		Anhydrite Ca(OH) ₂ CaO	Anhydrite Ca(OH) ₂ CaO	Anhydrite Ca(OH) ₂ CaO Calcite	Ca(OH) ₂ CaO Calcite

Evidence for the instability of anhydrite at 1500°C is given by the lack of detection of this mineral using either CCSEM or XRD. Most of the anhydrite resulted from the reaction of gas phase SO₂ with surface calcium oxide or calcium silicate. The PSD of the Ca(min.)-Si-S ash along with the synthetic coal minerals showed more mineral coalescence with increasing temperature (Figure 24). This indicates that the quartz and calcite particles locked within the synthetic coal matrix coalesced at higher temperatures, producing large ash particles that were derived from several mineral grains within a single coal particle.

Composition of the Ca(org.)-Si-S ash samples shows evidence of more calcium reacting on the surface of quartz particles rather than being captured on the interior (Table 7). The surface CCSEM analysis indicates more reaction to form amorphous calcium silicate at 1500°C. The PSDs for this system show the 900°C ash to be the largest (Figure 25). This indicates that the organically associated calcium reacts with the quartz within the synthetic coal particle in a manner that is different from the calcite, because instead of causing the least coalescence at the lower temperature, there is actually more (Figure 25). This effect may be due to higher reactivity of the char matrix at 900°C for the organic calcium mixture, as compared to the calcite mixture; therefore, more melting and interaction occurred between the quartz grains, causing a larger PSD to result. Measured reaction rates and corresponding particle temperatures were much greater for the Ca(org.)-Si-S system as compared to the Ca(min.)-Si-S at 900°C. The carbon conversion versus residence times for the Ca(org.)-Si-S and Ca(min.)-Si-S have been previously given in Figures 22 and 23.

Figure 24. Particle-size distribution of minerals in Ca(min.)-Si-S coal (determined using CCSEM) and fly ash (determined using Malvern analysis).

TABLE 7

Mineral and Amorphous Phase Composition of
Ca(org.)-Si-S Synthetic Coal and Fly Ash (wt%)

Mineral/Phase	Syn. Coal	Fly Ash			
		900°C	1100°C	1300°C	1500°C
CCSEM Cross-Section Analysis					
Quartz	92.9	82.6	89.2	92.8	90.4
Calcite/CaO	1.6	0.0	0.1	0.1	0.1
Ca-Silicate	0.1	4.2	4.6	4.6	4.2
Gypsum/Anhydrite	0.0	0.6	0.1	0.0	0.0
Ca-Si-S Mixture	2.1	4.1	1.6	1.3	1.5
CCSEM Surface Analysis					
Quartz	--	78.2	85.2	86.8	79.2
Calcite/CaO	--	0.0	0.1	0.3	0.1
Ca-Silicate	--	10.9	10.6	11.2	11.8
Gypsum/Anhydrite	--	1.9	0.3	0.0	4.6
Ca-Si-S Mixture	--	6.1	2.7	1.2	3.4
XRD Bulk Analysis					
Major	Quartz	Quartz		Quartz	
Minor		Anhydrite		CaO

Figure 25. Particle-size distribution of minerals in Ca(org.)-Si-S coal (determined using CCSEM) and fly ash (determined using Malvern analysis).

The Na(org.)-Si-S system, summarized in Table 8, produced lower levels of quartz and increasing levels of sodium sulfate and amorphous sodium silicate at lower temperatures (900° and 1100°C). Bulk compositions based on CCSEM data for Na, Si, and S show decreases in the Na and S and increases in the Si with increased temperature. Phases in the Na-Si-S mixture, as identified by CCSEM, contained Si and S as either amorphous sodium silicate or sodium sulfate. XRD did confirm the presence of a sodium-carbonate-sulfate mineral in the 900°C ash. The presence of the sodium-containing phases at lower temperatures was due to their greater stability at the lower temperatures. With increased temperature, sodium and sulfur become unstable and enter the vapor phase. Therefore, at 1500°C, virtually no Na, S, or amorphous Na-Si-S mixture was left in the ash (Table 8). The particle-size distribution of the Na(org.)-Si-S fly ashes (Figure 26) indicates that the 1500°C ash is much smaller than ash produced at the lower temperatures. This agrees with previous results from another experiment by Ludlow and others (16). The finer ash size was not the result of the fragmentation of quartz grains or the formation of fine sodium sulfates, but may have been the result of the burning char itself fragmenting. Another viable explanation is that agglomeration of the quartz particles was prohibited because the low melting point sodium silicates and sulfates, which act as "glue" to cause particle coalescence, were not able to remain stable at 1500°C. Sodium silicates and sulfates are generally stable at temperatures ranging between 800°-1000°C.

TABLE 8

Mineral and Amorphous Phase Composition of
Na(org.)-Si-S Synthetic Coal and Fly Ash (wt%)

Mineral/Phase	Syn. Coal	Fly Ash			
		900°C	1100°C	1300°C	1500°C
CCSEM Cross-Section Analysis					
Quartz	81.3	62.3	87.4	98.2	95.9
Na-Si-S Mixture	9.6	30.1	7.5	1.0	0.9
CCSEM Surface Analysis					
Quartz	81.3	86.4	97.3	94.8	96.0
Na Si-S Mixture	9.6	10.5	1.8	2.3	1.6
XRD Bulk Analysis					
Major	Quartz	Quartz		Quartz Cristobalite	Amorphous
Minor		Na ₆ CO ₃ (SO ₄) ₂			
Bulk Composition (XRF)					
Na*	17.0	27.3	7.3	2.9	0.5
Si	60.8	46.7	62.0	89.5	91.7
S*	15.6	18.8	21.1	1.2	1.0

* Expressed as normalized x-ray energy counts.

Figure 26. Particle-size distribution of minerals in Na(org.)-Si-S coal and ash.

The Fe(min)-Al-Si system compositions are given in Table 9. Decomposition of the pyrite is nearly complete at 900°C, with only small amounts of oxidized pyrrhotite remaining and the bulk of the iron converted to iron oxide. Some interaction of the iron oxide with the kaolinite to form an iron aluminosilicate phase is seen at 900°C. The degree of interaction remains relatively constant until 1500°C, whereupon the proportion of iron aluminosilicate approximately doubles. This behavior is consistent with the decomposition/oxidation behavior of pure pyrite in air at 900°C, which, as shown in Table 9, primarily forms iron oxide with a lesser amount of oxidized pyrrhotite. Although some interaction between the kaolinite and iron oxide occurs at lower temperature and long residence times, the lack of a fluxing agent discourages substantial interaction until, at 1500°C, the ash approaches the melting points of aluminosilicates (1500°C) and iron(III) oxide (1565°C).

The size distributions of the Fe(min.)-Al-Si coal and bulk filter ashes are shown in Figure 27. There is a small decrease in ash particle size of the 900°C bulk filter from that of the parent coal. This is attributed to some fragmentation of the pyrite as it oxidizes to form iron oxide. The remainder of the bulk filter ash samples at higher temperature have size distributions very similar to each other and intermediate between that of the 900°C ash and the parent coal.

4.4 Discussion

Interactions between the inorganic components of the synthetic coals were followed as a function of residence time and furnace temperature by analysis of individual mineral particles employing CCSEM. Samples analyzed were prepared by two techniques: cross-sectioning of particles embedded in an epoxy matrix, and dispersion on double-stick tape. The use of the two techniques provides complementary information as to the mineral composition of the particles. Cross-sectioning is more sensitive to bulk composition, while dispersion will more readily detect surface deposition on a particle.

TABLE 9
Mineral and Amorphous Phase Composition of
Fe(min.)-Al-Si Synthetic Coal and Fly Ash (wt%)

Minerals (CCSEM)	Syn. Coal	Bulk Filter 900°C	Bulk Filter 1100°C	Bulk Filter 1300°C	Bulk Filter 1500°C
Iron Oxide	0.6	39.2	33.4	35.9	35.8
Kaolinite	21.4	37.0	40.3	39.1	25.2
Fe Aluminosilicate	0.0	13.7	13.3	12.3	25.2
Aluminosilicate	1.2	1.0	2.4	4.5	5.7
Pyrite	65.6	0.0	0.0	0.0	0.0
Pyrrhotite	3.6	0.0	0.0	0.0	0.0
Oxidized Pyrrhotite	0.6	2.1	1.5	0.0	0.7
Other	3.5	2.5	3.2	4.1	3.1
Unknown	3.5	4.5	5.9	4.1	4.3

Figure 27. Particle-size distribution of minerals in Fe(min.)-Al-Si coal and ash.

Elemental analyses of about 1000 to 3000 mineral particles were obtained for each CCSEM analysis. Although CCSEM cannot identify specific mineral phases per se, the elemental percentages obtained can be used to infer interactions between the initial discrete inorganic components of the coals.

Since the synthetic coals under consideration contain simple three- and four-component inorganic systems, it is feasible to follow trends in particle composition even though individual compositions are not classifiable as particular mineral species, as has been done in previous studies of natural ash samples using CCSEM. Due to the large volume of composition data for individual ash particles, the data is presented as ternary scattergraphs of particle compositions versus percentage of three primary elemental components.

4.4.1 The Ca(min.)-Si-S System

Interaction of the inorganic components begins at 900°C, as shown in Figure 28. X-ray diffraction of the 900°C sample indicates the presence of calcium sulfate, as well as calcium oxide and $\text{Ca}(\text{OH})_2$ as minor crystalline phases, although essentially all particles contain <25% sulfur. Figure 28 also shows the particles contain a wide continuous range of calcium and silicon compositions. At higher temperatures, sulfur phases are not stable, as the maximum sulfur composition generally decreases to <10% at 1500°C. The Ca(min.)-Si-S system shows the same broad range of calcium-silicon composition at the maximum temperature studied, as shown in Figure 29. Examination of the PSD data revealed a very slight increase in particle size with increasing temperature (Figure 24).

Figure 28. Composition of ash particles produced from Ca(min.)-Si-S at 900°C. Data from cross section of bulk filter ash.

Figure 29. Composition of ash particles produced from Ca(min.)-Si-S at 1500°C. Data from cross section of bulk filter ash.

4.4.2 The Ca(org.)-Si-S System

Due to the highly dispersed nature of the organic calcium in the synthetic coal, the organic calcium appears to react with the silica particle surface, as the coal matrix burns away. Higher levels of calcium are detected by the CCSEM on the surfaces of the particles. Although initially highly dispersed, the distributions of the organic calcium-silica-sulfur with increasing temperature are generally similar to those for the Ca(min.)-Si-S system. The major difference is the scarcity of calcium oxide and calcium-sulfur species. Some indication of a calcium-sulfur species is seen in the 900°C distribution in Figure 30. The presence of sulfated species at 1500°C was negligible, as illustrated in Figure 31. Particle-size distribution analysis showed an initial decrease in mean particle size from 900° to 1100°C, with little change in mean diameter thereafter (Figure 25).

4.4.3 The Na(org.)-Si-S System

Interaction of the ash components of the Na(org.)-Si-S coal is seen to occur at 900°C, as shown in Figure 32. Clusters of data points close to 100% Si and Na indicate the expected presence of silica and a pure sodium phase, probably Na_2O . Another cluster at 50%-75% Na and 25%-50% S is indicative of the formation of a sodium sulfate species. X-ray diffraction analysis of the ash does, in fact, confirm the presence of burkeite ($\text{Na}_6[\text{CO}_3][\text{SO}_4]_2$) as a minor crystalline phase. A significant number of points indicate interaction of Na, Si, and S across a wide compositional range.

There is a dramatic compositional change in the ash collected at 1100°C and higher temperatures. The intermediate compositions disappear, and the great majority of the particles now are comprised of >90% silicon and <10% sodium and sulfur. At 1500°C, essentially all the sodium and sulfur species are in the vapor phase, and very little interaction with the silica is observed. This is illustrated in Figure 33 and is indicative of the loss of sodium and sulfur by devolatilization. PSDs show a gradual decrease in mean particle size with increasing temperature, indicating that little or no mineral particle agglomeration occurred or that some fragmentation of the char particles occurred during combustion (Figure 26). Examination of the fly ash produced at high temperatures indicated that melting of the quartz grains had occurred.

4.4.4 The Fe(min.)-Al-Si System

The S-Fe-Si and Al-Fe-Si compositional diagrams of the raw Fe(min.)-Al-Si synthetic coal obtained from CCSEM analysis are shown in Figures 34 and 35, respectively. Figure 34 shows the iron and sulfur to be associated primarily as pyrite, and Figure 35 shows the aluminum and silica associated as kaolinite. The diagrams for the bulk filter ash produced at 900°C are shown in Figures 36 and 37. As shown, the sulfur has almost entirely disappeared to a level of less than 10%, and the iron is isolated primarily as an iron compound, probably iron oxide. The Al and Si are still clustered together as kaolinite, but with a small scattering of values up the midline of Figure 35, indicating some interaction with the iron to form iron aluminosilicates. Figures 38 and 39 of the ash at 1500°C are virtually identical to the corresponding diagrams at 900°C, with the exception of a slight broadening of the kaolinite cluster, indicating increasing interaction with the iron oxide at the higher temperature.

Figure 30. Composition of ash particles produced from Ca(org.)-Si-S at 900°C. Data from a cross section of the bulk filter ash.

Figure 31. Composition of ash particles produced from Ca(org.)-Si-S at 1500°C. Data from a cross section of the bulk filter ash.

Figure 32. Composition of ash particles produced from Na(org.)-Si-S at 900°C. Data from a cross section of the bulk filter ash.

Figure 33. Composition of ash particles produced from Na(org.)-Si-S at 1500°C. Data from a cross section of the bulk filter ash.

Figure 34. S-Fe-Si composition of Fe(min.)-Al-Si synthetic coal. Data from cross-section analysis.

Figure 35. Al-Fe-Si composition of Fe(min.)-Al-Si synthetic coal. Data from cross-section analysis.

Figure 36. S-Fe-Si composition of ash particles produced from Fe(min.)-Al-Si at 900°C. Data from a cross section of the bulk filter ash.

Figure 37. Al-Fe-Si composition of ash particles produced from Fe(min.)-Al-Si at 900°C. Data from a cross section of the bulk filter ash.

Figure 38. S-Fe-Si composition of ash particles produced from Fe(min.)-Al-Si at 1500°C. Data from a cross section of the bulk filter ash.

Figure 39. Al-Fe-Si composition of ash particles produced from Fe(min.)-Al-Si at 1500°C. Data from a cross section of the bulk filter ash.

4.5 Combustion Testing of the Eagle Butte/Kentucky #9 Blend

4.5.1 Introduction

Reductions in SO₂ emissions from coal-fired power plants are required to meet increasingly stringent emission standards. One of the methods used to achieve lower emissions is to blend coals. Blending can reduce the total sulfur content of an eastern high-sulfur coal boiler fuel by diluting with a lower-sulfur western coal, but not without complications. The distribution of inorganic components in the western subbituminous coals differs significantly from eastern bituminous coals. Subbituminous coals contain high levels of organically associated cations (Na, Ca, Mg). Upon combustion, these organically associated species form small particles that are very reactive fluxing agents and reduce the viscosity of liquid phases responsible for some slagging and fouling problems.

In addition, these alkali and alkaline earth components can become sulfated, causing SO₂ capture, but possibly also causing backpass fouling on superheater surfaces. One approach to predict the ash behavior of blended coals is to generate experimental fly ash from the coals and the blend in a laboratory-scale DTF to simulate temperatures and particle residence conditions in a full-scale boiler. The initial coals, blend, and fly ashes are analyzed using CCSEM and SEMPC. The closely controlled combustion experiments and detailed analyses provide insights into ash behavior and the effects of coal blending on combustion systems.

4.5.2 Methods

The two coals selected for the experiment were 1) Kentucky #9, a high-sulfur eastern bituminous coal; and 2) Eagle Butte, a low-sulfur western subbituminous coal high in calcium. A blend ratio of 70% Eagle Butte and 30% Kentucky #9 was chosen on the basis of sulfur dioxide compliance levels. This ratio considers both dilution of the high-sulfur coal and sulfur capture by calcium contained in the western coal.

4.5.2.1 Eagle Butte/Kentucky #9 Coal Blend Preparation

Approximately 1000 pounds of Eagle Butte and Kentucky #9 coal was obtained to prepare an Eagle Butte/Kentucky #9 blend. Each coal was crushed and pulverized separately to obtain an approximate 70% -200-mesh grind. Proximate/ultimate and ash analyses were performed on each of these parent coals to determine a blend ratio for testing. Based on the results of these analyses, a blend of 70% Eagle Butte/30% Kentucky #9 by weight was prepared.

The 70/30 Eagle Butte/Kentucky #9 blend was prepared by weighing out appropriate amounts of the two coals in a hopper. The 70/30 ratio was then placed in a revolving mixer to blend the two coals. The blend was split into five approximately 150- to 200-lb samples by using a five-way rotating splitter. One of the five splits was further riffled to obtain a 100-, 30-, and 1-lb sample, as well as samples for analysis and testing in the EERC DTF. All samples were stored in sealed containers purged with nitrogen. Malvern, proximate/ultimate, chemical fractionation, and ash analyses were performed on the coal blend.

4.5.2.2 Char and Fly Ash Production for Eagle Butte Kentucky #9 Blend

The 70/30 Eagle Butte/Kentucky #9 blend was injected into the DTF at a furnace temperature of 1500°C and collected at residence times of 0.05, 0.1, 0.2, 0.5, and 0.8 seconds to produce chars at various degrees of burnout and ultimately a carbon-free fly ash. Carbon dioxide and carbon monoxide levels were recorded during these runs to determine carbon conversion. TGA was performed on the ash collected for each of the tests.

Carbon conversion percentages were calculated for the Eagle Butte/Kentucky #9 blend tests performed in the DTF by the three methods described earlier. Carbon conversion comparisons at 1500°C furnace temperature are shown in Figure 40.

Fly ash production in the DTF of Eagle Butte/Kentucky #9 under air was performed at a furnace temperature of 1500°C and residence time of 2.6 seconds. The ash was collected on a bulk filter and submitted for analysis. The DTF run conditions used for the short residence time and fly ash production tests are shown in Table 10.

Figure 40. Carbon conversion determinations during the DTF combustion of Eagle Butte/Kentucky #9 blend. Three methods were used to make the determinations including a method which used on-line gas analyzers, a weight loss method, and a TGA method.

TABLE 10

DTF Run Conditions for Eagle Butte/Kentucky #9 Blend

Drop-Tube Furnace Carbon-Loss Tests																				
Test ID	Coal Type	Res Time (Sec)	DTF Temp (°C)	O ₂ (%) Init	Coal Feed Rate (g/m)	CO ₂ Act (%)	CO Act (%)	O ₂ Act (%)	Pri Flow (L/m)	Sec Flow (L/m)	Quench Flow (L/m)	Vac Flow (L/m)	CO ₂ Moles (min)	CO Moles (min)	Pb Press (mm Hg)	Amb. Temp. (°C)	Carbon Orig (%)	Carbon Conv. (%)	Coal Burned (%)	Comb. Conv. (%)
EB/KY-0191	70/30 BL	0.80	1500	21.0	0.098	2.92	0.0052	18.53	0.8	3.2	3.0	7.2	0.0046	0.000008	736.89	27.0	51.8	109.0	102.5	98.5
EB/KY-0291	70/30 BL	0.50	1500	21.0	0.094	2.95	0.0221	17.94	0.8	3.2	3.0	7.2	0.0047	0.000035	736.89	27.0	51.8	115.6	100.2	94.9
EB/KY-0391	70/30 BL	0.20	1500	21.0	0.090	2.17	0.1157	18.74	0.8	3.2	3.0	7.2	0.0034	0.000182	736.89	27.0	51.8	92.9	81.8	73.3
EB/KY-0491	70/30 BL	0.10	1500	21.0	0.092	1.92	0.1688	18.85	0.8	3.2	3.0	7.2	0.0030	0.000266	736.89	27.0	51.8	82.9	78.2	55.3
EB/KY-0591	70/30 BL	0.05	1500	21.0	0.100	1.74	0.2447	18.77	0.8	3.2	3.0	7.2	0.0028	0.000386	736.89	27.0	51.8	72.6	74.8	40.1
EB/KY-0691	70/30 BL	2.63	1500	21.0	0.084	2.37	0.0005	18.84	0.8	3.2	3.0	7.2	0.0038	0.000001	742.79	26.0	51.8	104.3	103.1	0.0
EB/KY-0791	70/30 BL	2.63	1500	21.0	0.084	2.72	0.0000	17.23	0.8	3.2	3.0	7.2	0.0043	0.000000	738.69	25.0	51.8	119.4	106.6	0.0

TABLE 11

Five-Stage Multicyclone Data and Exit Gas Composition Results for Eagle Butte/Kentucky #9 Blend Fly Ash Production

Run # CIT-EBKY9-0791		1					
Furnace Configuration: Slagging							
Coal Type		EB/KY#9 70/30 Blend	<div>Gas Composition</div>				
Coal Ash %	7.34	Nitrogen	78.44				
Coal Size (µm)	31.4	Oxygen	17.23				
Density (g/c³)	1.18	Carbon Monoxide	0.00				
Coal Fed (g)	6.3	Carbon Dioxide	2.72				
		Moisture	1.61				
Furnace Wall Temp (°C)	1530						
Cyclone Box Temp (°C)	101						
Ambient Temp (°C)	25	Run Time (min)	75				
Pb (mm Hg)	738.69	Max. Particle Size (µm)	31.4				
Vacuum (L/m)	7.2						
Viscosity (micropoise)	211.79						
	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Filter	Totals
MASS(g)	0.0626	0.0076	0.0206	0.0190	0.0304	0.0271	0.1673
PCT	37.42	4.54	12.31	11.36	18.17	16.20	100.00
D50 (µm)	17.11	14.79	8.90	5.55	2.19	16.20	

The six-stage cascade multicyclone collection device was used to aerodynamically size segregate ash produced from the blend in the DTF. The run conditions used for this test were a 1500°C furnace temperature and a residence time of 2.6 seconds. Table 11 shows the multicyclone and exit gas composition results from this test. Most of the fly ash mass (37%) was collected in Stage 1 of the multicyclone. This stage collected ash that had an aerodynamic diameter size average of 17 μm . The multicyclone filter had significant quantities of fly ash that were less than 2 μm , primarily due to the production of fine ash from the Eagle Butte coal.

Ash deposits were also grown under fouling conditions for the Eagle Butte, Kentucky #9, and Eagle Butte/Kentucky #9 blend in the optical DTF. The optical DTF deposition probe is designed to simulate a boiler tube typical of those found in full-scale utility boilers. The probe maintains a sacrificial sample coupon attached to the probe at a specific temperature by aspirating water and nitrogen into an inner shell housing the coupon. The coupon temperature can be varied over a broad temperature range by adjusting the mixture of nitrogen and water in the deposition probe. The deposition probe consists of inner and outer shells surrounding a sample coupon, all attached to a stainless steel tube. In the inner shell, a series of annular tubes carry nitrogen and water to and from the probe to cool it and also to help keep the outer shell cool. The inner shell is removable from the probe and extends the full length of the probe. The annular tubes are surrounded by an outer shell which is attached to the end of the probe. The outer shell is insulated to minimize temperature loss in the optical zone and to help prevent oxidation. The deposits are grown on a sample coupon attached to the end of the deposition probe. These sacrificial coupons can be machined from any desired metal. A constrictor is used to accelerate the gas flow to approximately 15 m/sec before it impinges on the coupon. The upper surface of the coupon is curved to match the radius of the probe. The probe accepts a thermocouple to provide temperature measurements.

Table 12 gives the furnace conditions for the deposits. The deposit morphology was determined by optical and SEM examinations. The chemical content of the bases and main portions of the deposits was determined using SEMPC analysis.

4.5.2.3 Coal, Char, and Ash Analysis Techniques

The CCSEM technique was used to analyze the original coal particles and the DTF-generated fly ash. This technique determines the size, shape, quantity, and composition of the mineral grains in coal (20). The chemical composition data obtained are used to classify particles into mineral or chemical categories. By inspection of simultaneously collected digital backscatter images, the mineral grains can be further classified as locked into or liberated from the coal particle. Chemical fractionation analysis (2) was used to determine the amount of organically bound elements in the Eagle Butte, Kentucky #9, and the Eagle Butte/Kentucky #9 blend.

The SEMPC technique was used to analyze the DTF-generated fly ash and deposits to determine detailed chemistry of the liquid phase and to derive the viscosity. This technique quantitatively determines the relative amounts of phases present in entrained ashes and deposits (3). The method involves microprobe analysis of a large number of random points in a polished cross

TABLE 12

Drop-Tube Furnace Parameters for Ash Deposits, Using Slagging Conditions			
Parameter	Eagle Butte	Kent. #9	Blend
Gas Flow per Minute:			
Primary Air	0.8	0.8	0.8
Secondary Air	3.2	3.2	3.2
Vacuum	7.2	7.2	7.2
Temperatures (°C):			
Preheater	1000	1000	1000
Furnace 1	1530	1530	1530
Furnace 2	1530	1530	1530
Optical Zone	1100	1100	1100
Substrate	525	535	530
Other Parameters:			
Coal Burned (g)	2.07	0.18	0.69
Feed Rate (g/min)	0.094	0.090	0.099
Run Duration (min)	22	2	7
Ash Fed (g)	0.0865	0.0256	0.053
Ash Collected (g)	0.0614	0.0155	0.0266
Ash Collected/fed (%)	70.98	60.56	50.19

section of a sample. The sample matrix-corrected compositions are classified into mineral or chemical categories based on various weight and molar ratios developed from stoichiometry of the phases. Points not classifiable into the phase categories are assumed to be amorphous and represent the liquid phase during deposition. Since the chemistry of the liquid phase is known, the viscosity can be calculated (22).

4.5.3 Coal Characterization

Table 13 gives the coal characteristics for the Eagle Butte and Kentucky #9 coals and the 70% Eagle Butte/30% Kentucky #9 blend. The ash content is greatest for the high-volatile bituminous Kentucky #9 coal as compared to the subbituminous Eagle Butte coal. The blend has an ash content intermediate between the two parent coals.

The proximate and ultimate analyses of the blend correspond extremely well to what would be predicted from a 70/30 mixture based on the analyses of the parent coals. It thus appears that the blending operation was quite successfully performed. The elemental content of the blend reported as oxide percents and the mineral composition of the blend also correspond closely to that calculated for a blend of 70% Eagle Butte and 30% Kentucky #9. The slightly higher iron and sulphur concentrations may be caused by the density and computational properties of the pyrite during the pulverizing and blending process.

TABLE 13

Analyses of As-Fired Fuels: Eagle Butte and Kentucky #9
X-Ray Fluorescence and Proximate/Ulimate Results (in weight percentages)

	EB	KY	Meas. EB/KY	Calc. EB/KY
<u>Proximate</u>				
Moisture	27.3	6.5	21.8	21.1
Volatile Matter	35.0	37.3	34.5	35.7
Fixed Carbon	33.5	42.3	36.3	36.1
Ash	4.2	13.8	7.3	7.1
Caloric Value	9,254	11,618	9,815	9,963
<u>Ultimate</u>				
Hydrogen	6.7	5.2	6.3	6.3
Carbon	51.8	63.7	53.8	55.4
Nitrogen	0.6	1.3	0.8	0.8
Sulfur	0.4	4.1	1.5	1.5
Oxygen	36.3	11.9	30.2	29.0
Ash	4.2	13.8	7.3	7.1
<u>Elemental Oxides</u>				
SiO ₂	29.1	44.2	36.5	37.9
Al ₂ O ₃	17.1	19.2	18.3	18.3
Fe ₂ O ₃	7.2	23.8	17.3	16.9
TiO ₂	1.5	0.6	1.0	1.0
P ₂ O ₅	0.9	0.5	0.7	0.7
CaO	31.4	7.5	19.2	17.4
MgO	11.0	1.5	4.0	5.4
Na ₂ O	1.4	0.8	1.4	1.0
K ₂ O	0.4	2.0	1.4	1.3
SO ₃	18.1	6.1	17.1	11.1
<u>Mineral Basis (from CCSEM)</u>				
Quartz	31.20	9.10	11.00	18.3
Iron Oxide	2.00	0.10	0.20	0.9
Periclase	0.00	0.00	0.00	0.0
Rutile	0.90	0.10	0.40	0.4
Alumina	0.00	0.00	0.00	0.0
Calcite	0.40	7.50	7.60	4.6
Dolomite	0.10	0.20	0.30	0.2
Ankerite	0.00	0.00	0.00	0.0
Kaolinite	30.50	11.40	12.80	19.3
Montmorillonite	1.90	3.20	2.60	2.7
K Al-Silicate	0.50	19.20	14.80	11.4
Fe Al-Silicate	0.10	0.80	0.90	0.5
Ca Al-Silicate	1.00	0.10	0.20	0.5
Na Al-Silicate	0.30	0.20	0.20	0.2
Aluminosilicate	2.60	1.20	0.80	1.8
Mixed Al-Silica	0.00	0.20	0.40	0.1
Fe Al-Silicate	0.00	0.00	0.00	0.0
Ca-Silicate	0.00	0.20	0.00	0.1
Ca Aluminate	0.00	0.00	0.00	0.0

TABLE 13 (continued)

	EB	KY	Meas. EB/KY	Calc. EB/KY
<u>Mineral Basis (from CCSEM) (continued)</u>				
Pyrite	11.30	36.80	38.90	26.2
Pyrrhotite	0.00	0.10	0.10	0.1
Oxidized Pyrrhotite	0.80	0.00	0.00	0.3
Gypsum	0.00	0.10	0.70	0.1
Barite	0.40	0.00	0.30	0.2
Apatite	0.00	0.40	0.00	0.2
Ca-Al-P	7.00	0.00	0.40	2.9
KCl	0.00	0.00	0.00	0.0
Gypsum/Barite	0.20	0.00	0.10	0.1
Gypsum/Al-Silicate	0.30	0.20	0.10	0.2
Si-Rich	1.40	3.00	1.70	2.3
Ca-Rich	0.00	0.20	0.10	0.1
Ca Si-Rich	0.00	0.00	0.00	0.0
Unknown	6.90	5.90	5.40	6.3

Major differences in mineral content are apparent between the parent coals in Table 13, as determined using CCSEM analysis. Major minerals in the Eagle Butte coal are quartz, kaolinite, and pyrite, while the Kentucky #9 coal has major amounts of pyrite, kaolinite, and K-aluminosilicates with little quartz. The blend mineral composition, primarily with the exception of pyrite, is approximately that expected.

PSDs of the mineral particles in the fuels (Figure 41) show the Eagle Butte coal to have the smallest mean particle size and Kentucky #9 coal to have the largest. The blend is closest in PSD to that of the Eagle Butte coal. Figure 42 shows an SEM image of the blend. The lighter-colored particles are Eagle Butte coal, while the darker particles are Kentucky #9 coal. The difference in brightness is due to the higher calcium content of the Eagle Butte coal, in which the calcium is highly dispersed as organically bound calcium ions (Table 14). Again, the blend compares well with the composition calculated for a 70% Eagle Butte/30% Kentucky #9 mixture. Detailed results of the chemical fractionation analyses for the coals are given in Appendix A.

4.5.4 Char and Fly Ash Characterization

The 70/30 Eagle Butte/Kentucky #9 blend was combusted in the DTF at a furnace temperature of 1500°C and residence times of 0.05, 0.10, 0.20, 0.50, and 0.80 seconds. The extracted chars were characterized by Malvern and CCSEM analysis. Table 15 gives the CCSEM-determined mineral composition as a function of residence time. The most significant change in mineral composition is the rapid decrease in pyrite concentration after 0.10 second, accompanied by a concurrent increase in the iron oxide concentration, arising from the decomposition of the pyrite. Little change in the intermediate pyrrhotite and oxidized pyrrhotite concentrations is seen. A similar rapid decomposition of pyrite was seen with the pyrite-silica-aluminum

Figure 41. CCSEM particle-size distribution of parent coals and 70/30 blend.

Figure 42. SEM photograph of 70/30 Eagle Butte/Kentucky #9 blend.

TABLE 14

Summary of Organically Bound Constituents in Eagle Butte and Kentucky #9 Coals
CIT Test Fuels (wt% coal basis)

	EB	KY #9	EB/KY	Calc. EB/KY
Silicon	0.00	0.00	0.00	0.00
Aluminum	0.27	0.08	0.24	0.21
Iron	0.13	0.60	0.41	0.27
Titanium	0.00	0.00	0.00	0.00
Phosphorus	0.00	0.07	0.03	0.02
Calcium	1.03	0.00	0.69	0.77
Magnesium	0.36	0.02	0.21	0.26
Sodium	0.04	0.06	0.07	0.05
Potassium	0.01	0.03	0.00	0.02
Total Org. Bound	1.84	0.86	1.65	1.56
Total % Ash	4.20	13.80	7.30	7.08

synthetic coal in an earlier section of this report. After 0.50 seconds, an increase of a few percent is seen in the concentration of Fe Al-silicate, indicating some interaction of the iron with the clay minerals present in the char.

As shown in Table 14, the majority of the calcium in the blend is present as organically bound calcium species. There is a substantial increase in Ca-Al-silicate and Ca-aluminate species with residence time, indicating that the organically bound calcium has coalesced onto the ash and is interacting with the silica and clay minerals as the organic portion of the char burns away.

The Malvern size analysis for the 70/30 Eagle Butte/Kentucky #9 blend and the chars is shown in Figure 43. The mean particle size increases at the shorter residence times from 0.01 to 0.50 seconds. This increase is probably due to the swelling of the Kentucky #9 portion of the blend. Subsequent combustion of the char at 0.50- and 0.8-second residence times causes the char mean size to decrease again. In contrast, the CCSEM sizing of mineral particles for the chars is shown in Figure 44. In this case, the size of the ash particles actually increases somewhat with increasing residence time, indicative of some agglomeration of the mineral matter.

A comparison can be made from the iron-alumina-silica ternary diagrams for the blend coal and blend fly ash shown in Figures 45 and 46. As is seen, the majority of interaction between mineral phases during the fly ash formation is a broadening of the composition of the original alumina-silica clays. Very little interaction of the iron with aluminum and silica is seen. This suggests that iron-rich particles arising primarily from the Kentucky #9 portion of the blend experience only limited interaction with the alumina-silica clays of the Eagle Butte portion of the blend.

Viscosity distributions of silicate liquid phases were constructed for the 70/30 Eagle Butte/Kentucky #9 fly ash, the fly ashes from the two parent coals, and a weighted 70-30 mixture derived from the viscosity distributions

TABLE 15

Drop-Tube Furnace Test Results of Blend Char and Fly Ash at 1500°C
Weight Percentages on a Mineral Basis

	3108 EB/KY #9 coal	3370 EB/KY #9 Char	3371 EB/KY # 9 Char	3372 EB/KY #9 Char	3373 EB/KY #9 Char	3374 EB/KY #9 Char	3375 EB/KY #9 Ash	Calc. EB/KY #9 Ash
		0.05 sec	0.1 sec	0.2 sec	0.5 sec	0.8 sec	bf-cx ^a	
Quartz	11.0	19.6	16.3	19.0	10.6	13.2	13.7	5.6
Iron Oxide	0.2	4.4	5.7	6.0	8.0	6.3	12.6	13.2
Periclase	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.4	0.5	0.1	0.2	0.1	0.1	0.3	0.3
Alumina	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0
Calcite	7.6	6.9	8.4	4.4	10.7	8.3	5.6	3.4
Dolomite	0.3	0.4	1.0	0.8	1.0	0.3	0.4	1.9
Ankerite	0.0	0.1	0.0	0.1	0.0	0.1	0.1	0.1
Kaolinite	12.8	17.2	13.0	14.7	16.6	12.0	11.1	4.2
Montmorillonite	2.6	4.5	2.0	5.9	3.2	4.0	6.7	6.3
K Al-Silicate	14.8	12.9	8.7	14.3	7.0	6.0	3.1	2.5
Fe Al-Silicate	0.9	0.3	0.4	0.6	2.0	2.8	2.3	8.8
Ca Al-Silicate	0.2	0.8	1.0	1.0	5.4	5.3	5.6	5.4
Na Al-Silicate	0.2	0.2	0.3	0.3	0.0	0.6	0.0	0.0
Aluminosilicate	0.8	2.2	0.8	2.6	2.4	2.5	2.9	2.2
Mixed Al-Silica	0.4	0.4	0.3	1.2	1.1	1.4	0.9	1.1
Fe-Silicate	0.0	0.1	0.1	0.0	1.2	0.1	1.6	0.6
Ca-Silicate	0.0	0.2	0.2	0.5	1.0	1.8	1.4	3.4
Ca-Aluminate	0.0	1.3	2.3	3.3	7.3	9.6	5.8	11.4
Pyrite	38.9	13.0	22.1	5.7	0.3	0.1	0.0	0.0
Pyrrhotite	0.1	0.8	1.5	0.6	0.0	0.0	0.0	0.0
Oxidized Pyrrhotite	0.0	1.7	1.4	0.5	0.3	0.2	0.1	0.0
Gypsum	0.7	0.4	0.1	0.4	0.2	0.0	0.0	0.0
Barite	0.3	0.2	0.1	0.0	0.0	0.0	0.0	0.0
Apatite	0.0	0.2	0.0	0.3	0.6	0.0	0.2	0.0
Ca-Al-P	0.4	0.0	0.1	0.1	0.0	0.0	0.0	0.0
KCl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum/Barite	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.0
Gypsum/Al-Silicate	0.1	0.1	0.0	0.1	0.1	0.2	0.4	0.1
Si-Rich	1.7	1.8	1.0	3.7	2.1	2.8	4.8	4.3
Ca-Rich	0.1	0.3	0.9	0.7	1.9	1.9	1.3	5.0
Ca Si-Rich	0.0	0.0	0.3	0.1	0.4	0.6	1.2	1.6
Unknown	5.4	9.7	11.8	12.9	15.9	19.6	17.9	18.9

^a Bulk filter cross section.

Figure 43. Malvern particle-size distribution of 70/30 Eagle Butte/Kentucky #9 chars.

Figure 44. CCSEM particle-size distribution of 70/30 Eagle Butte/Kentucky #9 chars.

Figure 45. Fe-Al-Si ternary diagram of the 70/30 Eagle Butte/Kentucky #9 blend coal.

Figure 46. Fe-Al-Si ternary diagram of the 70/30 Eagle Butte/Kentucky #9 blend fly ash.

of the two parent coals. A cumulative frequency plot of these four viscosity distributions is shown in Figure 47. It is seen that the fly ash from the parent Eagle Butte coal has the lowest viscosity distribution, and the fly ash from the parent Kentucky #9 coal has the highest. Viscosity distributions for the weighted mixture of the parent coals and the 70/30 Eagle Butte/Kentucky #9 blend fly ash are intermediate between the parent ash distributions. From this information, it can be deduced that the Eagle Butte fly ash tends to be the stickiest ash and the Kentucky #9 ash is the least sticky. When the parent coals were blended and fired in the DTF, their product ash was intermediate in viscosity distribution between that of the parent ash viscosity distributions. The blend distribution is actually intermediate between the weighted average of the parent fly ashes and the Kentucky #9 viscosity distribution. This may indicate that some limited interaction occurred between the inorganic constituents of the 70/30 Eagle Butte/Kentucky #9 blend during combustion in the DTF.

Viscosity distributions were also constructed for the bases and main portions of the deposits grown under fouling conditions for the two parent coals and the blend. Cumulative frequency plots of these viscosity distributions, along with calculated viscosity distributions based on a weighted average of the parent deposits, are shown in Figures 48 and 49. The viscosity distribution of the blend base deposit is significantly less than that calculated from the weighted average of the parent base deposits and is approximately the same as that of the Kentucky #9 parent base deposit viscosity distribution. Thus, the Kentucky #9 ash appears to dominate the portion of the deposit that forms first. In contrast, the viscosity distributions of the main deposits of the parent coals and the blend appear to be nearly the same.

The results of the viscosity calculations indicate that the blend is closer in viscosity distribution to that of the parent Kentucky #9, even though the blend coal is comprised of 70% Eagle Butte coal and only 30% Kentucky #9 coal. This indicates that a substantial reduction in sulfur emissions could be achieved by blending, with only moderate deviation of the ash viscosity from that of the parent Kentucky #9 ash.

Analysis of ashes generated in the DTF using fouling, fuel-rich conditions showed interesting variations with different fuel-air stoichiometric ratios. Ashes for each of the three coals, the Eagle Butte, the Kentucky #9, and the Eagle Butte/Kentucky #9 blend, were produced using a stoichiometric ratio of unity. The Fe-Al-Si synthetic coal was also combusted under similar conditions with a stoichiometric ratio of unity. For comparison, the stoichiometric ratio was varied for the blend; blend ash samples with stoichiometric ratios of 0.75 and 1.4 were also analyzed. Mineral compositions of each ash sample were determined using CCSEM, and are shown in Table 16. As would be expected, the synthetic coal ash has the simplest composition, containing primarily iron oxide, kaolinite, iron aluminosilicate, and aluminosilicate. For the Eagle Butte, Kentucky #9, and blend ash samples with stoichiometric ratios of unity, the composition of the blend is intermediate between that of the two parent coal ashes, with the exception of calcium aluminosilicate, which is higher in the blend than in either of the parent ashes. This discrepancy may be the result of the inclusion of one or more large calcium aluminosilicate particles in the blend ash analysis. In general, the intermediate composition of the blend ash corroborates the conclusions regarding coal blending discussed above.

Figure 47. Viscosity distributions of Eagle Butte, Kentucky #9, and blend ashes.

Figure 48. Eagle Butte and Kentucky #9 viscosity distributions for base deposits.

Figure 49. Eagle Butte and Kentucky #9 viscosity distributions for main deposits.

Comparison of blend ashes produced at varied fuel/air stoichiometric ratios indicates several different trends among the mineral categories. Weight percentages of Ca-Al-silicate and ankerite are directly proportional to the stoichiometric ratio. The minerals calcite, K Al-silicate, Fe Al-silicate, and Ca silicate show the opposite trend, with concentrations that are inversely proportional to the changes in stoichiometric ratio. Several other minerals, including iron oxide, dolomite, aluminosilicate, and Ca aluminate, are present in greatest concentrations for a stoichiometric ratio of unity, and decrease when the ratio is increased or decreased. The kaolinite, gypsum/Al-silicate, and Si-rich categories are present in the smallest weight percentages for a stoichiometric ratio of unity, and increase in concentration as the ratio is varied. The fact that minerals of similar chemical composition (i.e., Ca-bearing, silica-bearing, etc.) exhibit different trends as the stoichiometric ratio is varied suggests that these ratios have a complex effect on mineral transformation processes. The fuel-rich conditions used during the experiments suggest that the coal may not have been completely combusted, thus preventing the inorganic transformations from proceeding to completion. The varied compositional trends observed in the CCSEM data may thus be understood as representative of a range of partially complete transformations.

TABLE 16

CCSEM Results for Ashes Produced Under Fuel-Rich, Fouling Conditions
Area Percent Mineral Basis (SR = stoichiometric ratio)

Mineral	Fe-Al-Si SR = 1	Eagle Butte SR = 1	KY #9 SR = 1	Blend SR = 1	Blend SR = 0.75	Blend SR = 1.4	Eagle Butte O-rich	KY #9 O-rich	Blend O-rich
Quartz	0.3	4.5	13.8	9.7	9.9	6.1	4.6	7.3	9.3
Iron oxide	14.8	0.1	5.8	1.9	0.1	0.4	0.5	4.8	1.0
Rutile	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.0	0.0
Alumina	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.1	0.0
Calcite	0.0	0.9	3.6	1.5	1.7	1.1	0.6	1.0	0.9
Dolomite	0.0	12.1	0.0	3.7	2.6	1.0	2.9	0.0	0.0
Ankerite	0.0	0.4	0.0	0.6	0.1	1.1	0.4	0.2	0.3
Kaolinite	36.3	0.5	16.6	6.8	12.0	9.1	0.3	10.8	5.1
Montmorillonite	1.9	0.0	12.4	4.9	5.8	4.8	0.1	6.3	2.5
K Al-Silicate	0.0	0.1	9.1	2.0	5.3	1.6	0.0	4.2	1.3
Fe Al-Silicate	22.0	0.0	6.2	1.4	2.0	1.3	0.0	7.3	1.5
Ca Al-Silicate	0.5	7.0	3.0	11.4	8.4	14.2	6.4	2.8	8.1
Na Al-Silicate	0.3	5.0	1.4	1.5	2.0	4.7	3.7	0.0	0.0
Aluminosilicate	12.6	0.1	3.5	2.1	1.7	1.8	0.5	4.3	1.0
Mixed Al-Silicate	0.2	2.1	3.1	2.5	2.5	2.2	1.1	5.9	3.0
Fe-Silicate	0.2	0.0	0.8	0.1	0.0	0.1	0.0	0.5	0.0
Ca-Silicate	0.0	2.3	0.9	1.1	1.9	0.9	4.7	0.1	1.8
Ca Aluminate	0.0	13.5	0.2	6.3	3.7	4.2	17.1	0.0	1.5
Pyrite	0.0	--	0.1	0.0	3.3	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	--	0.1	0.0	1.9	0.0	0.0	0.0	0.0
Oxidized Pyrrhotite	0.8	0.0	0.3	0.0	0.5	0.0	0.0	0.4	0.3
Gypsum	0.0	0.0	0.4	0.0	0.3	0.5	0.0	2.1	3.5
Apatite	0.2	0.0	0.0	0.1	0.0	0.1	0.0	0.1	0.0
Ca-Al-P	0.0	0.0	0.0	0.0	0.4	0.1	0.0	0.0	0.0
Gypsum/Al-Silicate	0.0	0.3	0.1	0.9	1.6	2.6	5.5	0.4	3.5
Si-Rich	1.0	0.4	5.6	2.7	3.8	3.1	0.9	6.3	3.3
Ca-Rich	0.0	1.7	1.7	1.0	1.1	1.2	3.8	0.7	0.4
Ca Si-Rich	0.0	0.3	0.1	0.5	0.6	0.3	1.6	0.2	0.7
Unknown	8.9	48.4	11.1	36.7	27.0	37.5	45.1	34.3	50.9
Totals	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

XRD analysis of the blend ash samples produced at three different stoichiometric ratios shows that two ferrite spinel, $(\text{Mg,Fe})(\text{Fe,Al})_2\text{O}_4$, a reduced phase, is a major component of the two ashes produced at stoichiometric ratios of 1.4 and 1.0. In contrast, ferrite spinel is present only as a minor phase in the ash produced using a stoichiometric ratio of 0.75. This variation suggests a reducing environment was present at the lowest stoichiometric ratio, preventing the oxidation of pyrite and pyrrhotite that would otherwise occur.

PSDs for the ashes generated under fuel-rich, fouling conditions are shown in Figures 50 and 51. Figure 50 displays size distributions for four different ashes, all produced using a fuel/air stoichiometric ratio of unity. Distributions for the synthetic Fe-Al-Si ash and for the Eagle Butte ash both peak in the 2.2- to 4.6- μm size range. The distribution of the Kentucky #9 ash peaks in the 10- to 22- μm size range, and the blend ash peaks in the 4.6- to 10- μm range. Each size distribution is unimodal. The positioning of the peak for the blend size distribution in between that of the two parent coal ashes is expected based on the behavior of the blend as a weighted mixture. If the two components of the blend behaved independently, a bimodal size distribution would result.

Size distributions for Eagle Butte/Kentucky #9 blend ash produced under three different fuel/air stoichiometric ratios are presented in Figure 51. All three size distributions are unimodal. The distribution for a ratio of unity peaks in the 4.6- to 10- μm size range. The distributions for ratios of 0.75 and 1.4 both peak in the range 2.2- to 4.6 μm . The ash produced using a ratio of 1.4 has the narrowest size distribution (i.e., the greatest percentage of mass in the peak range), whereas the ash produced using a stoichiometric ratio of 0.75 has the broadest size distribution. These data suggest that a greater stoichiometric ratio leads to a more uniform ash formation process, yielding a greater concentration of particles in a single size range.

4.5.5 Conclusions

The analyses of the parent coals and the 70/30 Eagle Butte/Kentucky #9 blend indicates that the blending operation was quite successful, since most of the blend physical properties are very close to a weighted average of those of the parent coals. Pyrite was seen to decompose to iron oxide early in the combustion process, with some subsequent interaction of the iron with clay minerals to form Fe-Al-silicate species. The calculated viscosity distribution of the blend ash is intermediate between those calculated for the ashes of the parent coals, and similar to a simple weighted average of the viscosity distributions of the parent coal ashes.

Carbon conversion results from the gas analysis and weight methods indicate that the Eagle Butte/Kentucky #9 blend was 100% combusted by 0.5 seconds with a furnace temperature of 1500°C. TGA results indicate that combustion of the coal blend was almost complete by 0.8 seconds. The gas analysis and weight methods of carbon conversion show conversions higher than 100% for the longer residence times. In general, the different methods of conversion follow the same trends of conversion, with the TGA method showing lower conversion percentages than the other two methods at all residence times.

Figure 50. Size distributions for ash samples produced in the DTF, using fuel-rich, fouling conditions with stoichiometric ratios of unity.

Figure 51. Size distributions for Eagle Butte/Kentucky #9 ash samples produced in the DTF, using fuel-rich, fouling conditions with varied stoichiometric ratios.

A blend of 70% Wyoming Eagle Butte low-sulfur (<1% mf) subbituminous coal and 30% Kentucky #9 high-sulfur (4% mf) bituminous coal was analyzed using CCSEM. Experimental fly ash was generated in the DTF using a gas temperature of 1500°C and residence time of about 2.5 seconds (slagging conditions). The fly ash was analyzed using SEMPC and CCSEM. Coal analyses revealed that the blending operation was quite successful since the physical and chemical components are nearly weighted averages of the components in the parent coals. The fly ash revealed little interaction between the mineral components of the two different coals. The viscosity distributions of liquid phases in the blend fly ash under slagging conditions were intermediate between those of the weighted average of the parent fly ashes and the Kentucky #9 ash.

The bases and main portions of ash deposits grown under fouling conditions were produced and then analyzed using SEMPC. The viscosity distribution of the base deposit of the blend was less than that calculated for the weighted average of the parent base deposits, and approximately identical to that of the Kentucky #9 base deposit. The viscosity distributions of the main portion of the deposits were similar for both parent coals and for the blend. Although only 30% of the coal blend is Kentucky #9, it appears to dominate the ash viscosity distributions more than expected based on a calculated weighted average of the parent ash viscosity distributions.

Iron-rich particles derived from the pyrite in the Kentucky #9 coal experienced only limited interaction with aluminosilicates, most of which had sources in the Kentucky #9.

5.0 TASK 3: DEVELOPMENT OF ANALYTICAL METHODS

The objective of Task 3 was to enable a precise characterization of the minerals present in pulverized coals and to coordinate an effort between laboratories performing CCSEM analysis on coal in order to develop a consistent methodology. Standard methods of coal mineral characterization do not provide the level of detail needed to predict the interactions that take place during combustion. The characteristics of minerals which affect their behavior during combustion include 1) chemical composition, 2) size, 3) association of the minerals with the coal matrix, 4) associations among minerals, and 5) mineral shape. Presently, coal minerals are characterized using a CCSEM, which yields mineral compositions and sizes. The goals of Task 3 were to enhance the present methodology to include other significant mineral characteristics, such as mineral associations, mineral shapes or morphology, the relationship of the minerals to the coal matrix, and the analysis of individual submicron particles. CCSEM was used together with an automated image acquisition and characterization program to provide the needed data. One resultant methodology is a PBPSEM technique. A final objective of this task focused on standardizing CCSEM as a viable interlaboratory technique. A round-robin analysis of coal was initiated for the purpose of providing a sound basis for different laboratories to compare CCSEM results. A possible result of the round-robin CCSEM work is certification of the CCSEM method through an appropriate professional society.

5.1 Description of JEOL/Tracor Northern System

The SEM/microprobe system at the EERC consists of a JEOL 35U scanning electron microscope/microprobe, a GW Electronics backscattered electron detector, an ultrathin window energy-dispersive x-ray spectrometer, a wavelength-dispersive x-ray spectrometer, digital beam control, a Tracor-Northern 5600 x-ray microanalyzer control system, a Tracor-Northern 8500 image analyzer, and stage automation. The Tracor-Northern 5600 is interfaced with a personal computer system for advanced data manipulation and storage.

The key components of the SEM system that make it possible to image, size, and analyze inorganic particles include the backscattered electron detector, digital beam control, and the ultrathin window energy-dispersive x-ray spectrometer. The Tracor-Northern 8500 image analysis system can perform automated acquisition, storage, and processing of images from the SEM.

The CCSEM analysis technique uses backscattered electron imaging (BEI) and EDS to analyze minerals. Since the mineral or ash particles appear brighter in BEI relative to the lower atomic number background of the matrix, a distinction can be made between coal, epoxy, and mineral grains. Using the Tracor-Northern particle recognition and characterization program, the electron beam scans over the field of view to locate bright inclusions that correspond to mineral or ash species. On finding a bright inclusion, the beam performs eight diameter measurements on the inclusion, finds the center of the inclusion, and collects an EDS for 5 seconds. The system is configured to detect 12 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Ba, and Ti. Data from the CCSEM analysis are transferred simultaneously to a personal computer where they are stored on disk. The following essential information for each particle analyzed is stored: size, area, perimeter, chemical composition (x-ray count percentages), coordinates of location on the sample surface, frame number, and number of energy-photon counts. Software developed at the EERC classifies the minerals into categories based on size and composition (20).

ADEM Description

In order to facilitate the development of fully automated SEM analysis routines using image analysis, an ADEM was purchased and is now in use. The Tracor Northern ADEM is the first SEM to obtain total system automation and computer control of all system parameters. The ADEM completely integrates analytical EDS and digital image processing (Figure 52). This totally automated and integrated system is being used for further developments in the CCSEM program. The JEOL/Tracor Northern system is not capable of changing beam parameters such as magnification, focus, and operating voltages in an automated, computer-controlled fashion. The control and monitoring of these parameters is integral for planned CCSEM developments outlined in the description of Subtask B, CCSEM Automation and Development. The ADEM provides further capabilities to the CCSEM development program because it is capable of the automated analysis of multiple samples, which greatly increases the efficiency of the entire system and the amount of beam time available for research and technique development. In addition, the ADEM is able to image objects as small as 0.1 μm in diameter, allowing analysis of the smallest ash particles.

Although CCSEM has been used extensively to analyze coal mineralogy, little information is available to evaluate the performance characteristics (i.e., precision, accuracy, sensitivity, and limitations) of this important analytical method. The evaluation process has been impeded because there are no certified coal mineral standards available, and there are only a limited number of laboratories employing CCSEM available to perform collaborative testing. Casuccio and others (34) and Vleeskens and Hamburg (35) conducted an interlaboratory testing study involving six laboratories to evaluate repeatability and reproducibility. The data from four of the participating laboratories were evaluated. Two of these participants used the same instrument and operating conditions. The authors attributed the majority of interlaboratory variability observed to differences in x-ray detector performance characteristics and backscattered electron (BSE) video threshold settings.

This report summarizes the objectives, organization, and plans of a round-robin testing study designed to investigate and evaluate the CCSEM method of quantitative coal mineral analysis. Argonne Premium Coal Samples Wyodak-Anderson, Illinois No. 6, and Pittsburgh No. 8 are potential candidates for analysis. Initial analyses will be performed by the EERC to ascertain the suitability of these coals for the round-robin testing. The data obtained will be used to optimize the method and to further develop a CCSEM procedure.

5.2.2 Background

5.2.2.1 General Description of the CCSEM Method

This section briefly describes the CCSEM procedures of collecting and presenting data that are common to the majority of laboratories participating in the study. Coals to be analyzed are mounted in a medium (e.g., epoxy, carnauba wax), cross-sectioned, polished, and carbon-coated. An SEM operating in the BSE imaging mode is programmed to scan preselected areas of the polished coal surface. Mineral particles are automatically detected by an increase in the BSE signal above a preset video threshold. The electron microbeam locates the center of the particle, measures its size, and collects an energy dispersive x-ray spectrum. Regions-of-interest in the spectra are defined to measure the characteristic x-ray emission intensities of common, mineral-forming, major and minor elements. The analyses are classified into various mineral categories, based on relative elemental intensities and stoichiometric criteria. The classified particles are allocated according to cross-sectional diameter into size intervals. The analysis is performed at different magnifications to provide the image resolution necessary to obtain information on the distribution of minerals in different size classes. The results are summarized in terms of the number and proportions of various mineral classification categories in their respective size intervals.

5.2.2.2 Factors Affecting CCSEM Results

Instrumentation characteristics, operating parameters, and procedures that are unique to the participating laboratories will affect the intra- and interlaboratory agreement of CCSEM analysis results. Critical factors are presented in Table 17. Many of these were identified and tabulated by Birk (36).

TABLE 17

Factors Affecting CCSEM Analysis Results of Coal

Coal Sample:	<ul style="list-style-type: none"> • Coal Heterogeneity • Coal Rank • Mineral Particle Size • Mineral Intergrowths • Representative Collection
Preparation:	<ul style="list-style-type: none"> • Comminution Method • Mounting Medium • Mounting Method • Polishing Method • Conductive Coating Method
Instrumentation:	<ul style="list-style-type: none"> • Operating Parameters (Beam Voltage/Current, Magnification, etc.) • Electron Beam Stability • Geometry (Working Distance, X-Ray Takeoff Angle, etc.) • X-Ray Detector Sensitivity and Efficiency • BSE Detector Sensitivity • Beam Control
Data Collection and Reduction:	<ul style="list-style-type: none"> • X-Ray Spectral Acquisition Time • Elements Analyzed • Magnification(s) • Number of Particles Analyzed per Mag. • Amount of Area Analyzed • Video-Sampling Signal Value • BSE Video Signal Threshold • Particle-Size Intervals • Mineral/Chemical Definitions • Classification Categories • Calculation Methods

In this study, the interlaboratory variability originating from coal sampling and preparation is virtually eliminated because all participating laboratories will analyze identically prepared samples. Samples were prepared, under the supervision of Dr. Paul Gottlieb of CSIRO, by mixing the coals with crushed graphite and epoxy, and then casting the mixture into 30-mm-diameter pellets. A major concern, however, is the variability resulting from differences in instrumentation performance characteristics, operating parameters, data acquisition parameters, and data reduction procedures. The experimental conditions routinely employed at various laboratories are summarized in Table 18.

5.2.3 Objectives and Organization of the CCSEM Round-Robin Study

5.2.3.1 Introduction

A three-task plan has been devised to achieve the objectives of this study (Table 19). The first task is designed to produce a database of

TABLE 18

CCSEM Experimental Conditions

Laboratory	Ames	EERC	KY	ECN	Sandia
Accelerating Voltage (kV)	15	15	20	20	15
Probe Current (nA)	0.7	0.6	0.7	0.6	variable
Magnifications (x)	50/200/500	50/240/500	20/100/500	50/150/450	50/200 or 300/500
Spectral Acquire Time (sec)	3	5	2	2	10
SEM	JEOL 840A	JEOL JSM-35	ETEC-Autoscan	JEOL 840	JEOL 733 or JEOL JSM-35
X-Ray Analyzer	Kevex Delta-V	TN-5500	TN-2000	TN-2000	TN-5502
Software	Kevex Feature Analysis, LeMont Scientific Line Scan Analysis	PRC* PartChar ^{©**}	CMA*	CMA	CMA PRC

* Coal Mineral Analysis and Particle Recognition and Characterization computer programs marketed by NORAN Instruments, Inc. (formally Tracor Northern) (37).

** Particle Characterization computer program developed by the Energy and Environmental Research Center.

TABLE 19

CCSEM Round-Robin Task Objectives

Task 1: Initial CCSEM Round-Robin Testing

Compile a database of interlaboratory CCSEM analyses acquired on identical coal samples using documented analysis parameters and procedures.

Task 2: Evaluation and Investigation of the Round-Robin Analysis Results

- (a) Identify sources of intra- and interlaboratory variability.
- (b) Develop a CCSEM procedure for quantifying coal mineralogy based on recommendations accepted by a consensus of the round-robin participants.
- (c) Assess the performance characteristics (i.e., repeatability and reproducibility) of the CCSEM method.

Task 3: Reporting of CCSEM Round-Robin Test Study

Prepare a final report summarizing the CCSEM round-robin test results and recommendations of the participants.

interlaboratory CCSEM analysis results collected under very general guidelines. The seven laboratories identified above are anticipated to contribute to this database. In the second task, a CCSEM procedure will be developed based on a detailed analysis of the round-robin database in conjunction with the recommendations of participants. The third task involves the reporting of results and recommendations of the round-robin study. These tasks are subdivided into subtasks and described in the subsequent sections of this report.

5.2.3.2 Contacted Personnel and Laboratories

Dr. Harry ten Brink and Dr. G. Hamburg, Netherlands Energy Research Foundation ECN, 1755 ZG Petten, The Netherlands, Telephone: 31-2-246-3489, Fax: 31-2-246-4480.

Dr. Gary Casuccio, R.J. Lee Group, Monroeville, PA 15146, USA, Telephone: (412) 325-1776, Fax: (412) 733-1799.

Dr. Paul Gottlieb, CSIRO Division of Mineral & Process Engineering, Clayton, Victoria 3168, Australia, Telephone: 61-3-541-1222, Fax: 61-3-562-8919.

Dr. Gerry Huffman, University of Kentucky, Lexington, KY 40506, USA, Telephone: (606) 257-4027, Fax: (606) 258-1049.

Dr. Warren Straszheim, Ames Laboratory, Institute for Physical Research & Technology, Iowa State University, Ames, IA 50011, USA, Telephone: (515) 294-8187, Fax: (515) 294-3091.

Dr. Nancy Yang, Sandia National Laboratories, Combustion Research Facility,
Livermore, CA 94550, USA, Telephone: (510) 294-2680, Fax: (501) 294-
1004.

Mr. Chris Zygarlicke, Energy & Environmental Research Center (EERC),
University of North Dakota, Grand Forks, ND 58202, USA, Telephone:
(701) 777-5000, Fax: (701) 777-5181.

5.2.3.3 Task 1: CCSEM Round-Robin Testing

5.2.3.3.1 Sample Description, Preparation, and Distribution

Ampules of 100-mesh Wyodak-Anderson subbituminous coal, Illinois No. 6 high-volatile bituminous coal, and Pittsburgh No. 8 high volatile bituminous coal were obtained from the Argonne Premium Coal Sample Program. Argonne Premium Coal Samples were selected because their physical and chemical properties are well characterized (23,24,28,38-41). Samples were prepared, under the supervision of Dr. Paul Gottlieb of CSIRO, by mixing the coals with crushed graphite and epoxy, and then casting the mixture into 30-mm-diameter pellets. The sample surfaces were polished and coated with a thin conductive layer of carbon. A total of five CCSEM analyses will be performed by each participating laboratory on the three coals (Table 20). A polished epoxy mount of the Illinois No. 6 coal and the Wyodak-Anderson coal will be routed to each participating laboratory according to the schedule in Table 21. Participants will also receive an epoxy mount of the Pittsburgh No. 8 coal. The EERC will analyze these coals initially to determine their suitability for the round-robin study.

5.2.3.3.2 Analysis Guidelines

The information in Tables 17 and 18 was used to formulate analysis guidelines for the tests, as listed in Table 22. The analyses are to be performed at three magnifications of 500x, 240x, and 50x corresponding to particle diameter range limits of 1.0-4.6 μm , 4.6-22 μm , and 22-100 μm , respectively, with at least 1000 particles analyzed at each magnification, or

TABLE 20

Round-Robin Test Matrix

Coal	Sample Identification	Laboratory	Number of Analyses
Illinois No. 6	COLH064D	All	1
Wyodak-Anderson	COLH063D	All	1
Pittsburgh No. 8	COLH062F	Ames	3
"	COLH062C	CSIRO	3
"	COLH062E	ECN	3
"	COLH062D	EERC	3
"	COLH062G	Kentucky	3
"	COLH062H	Sandia	3
"	COLH062B	R.J. Lee	3

TABLE 21

Sample Distribution and Analysis Schedule		
Suggested Sample Receiving Dates and Analysis Reporting Dates		
Laboratory	Pittsburgh No. 8 Coal	Illinois No. 6 and Wyodak-Anderson Coals
EERC	June 8 - July 8, 1992	June 1 - June 14, 1992
ECN	June 8 - July 8, 1992	June 15 - June 29, 1992
Ames	June 8 - July 8, 1992	June 30 - July 14, 1992
Kentucky	June 8 - July 8, 1992	July 15 - July 29, 1992
R.J. Lee	June 8 - July 8, 1992	July 30 - August 13, 1992
CSIRO	June 8 - July 8, 1992	August 14 - August 28, 1992
Sandia	June 8 - July 8, 1992	August 31 - Sept. 14, 1992

Note: After completing the analyses, the laboratories will immediately return the samples to Mr. Chris Zygarlicke, Energy and Environmental Research Center, University of North Dakota, Box 8213, University Station, Grand Forks, ND 58202.

TABLE 22

Round-Robin CCSEM Analysis Guidelines	
Operating Parameters:	
Accelerating Voltage (kV)	15 or 20
Probe Current (nA)	N.S.*
Magnifications (x)	50/240/500
Data Acquisition Parameters:	
Number of Particles Analyzed per Magnification	1000
Particle Diameter Range Limits (μm)	1.0-4.6 @ 500x 4.6-22 @ 240x 22-100 @ 50x
Spectral Acquisition Time (sec)	2-10
Video Sampling Signal (Dimensionless Quantity)	N.S.
BSE Video Threshold (Dimensionless Quantity)	N.S.
Data Reduction Parameters:	
Classification Categories	N.S.
Category Definitions	N.S.
Particle-Size Intervals	N.S.

* Not specified.

until the entire sample is analyzed. These operating and data acquisition guidelines are specifically designed for the quantitative analysis of mineral particles as small as one micron in diameter. The implementation of these guidelines will reduce interlaboratory variability resulting from differences in operating parameters, data acquisition parameters, and counting statistics. Critical parameters that are not specified are the BSE video threshold setting and the video sampling signal value.

5.2.3.3.3 Analysis Reporting Requirements

The intra- and interlaboratory agreement of CCSEM results will be assessed based on the measured area fractions of individual mineral/chemical classification categories. Specific information about critical operating, data acquisition, and data reduction procedures must also be reported by each participant to facilitate the investigation of the method and the interlaboratory comparison of results. The minimum requirements for reporting each analysis are as follows:

1. Information enumerated in Table 22.
2. Analysis report containing information on the measured area fractions of individual mineral/chemical classification categories.
3. A data file saved to computer disk (3½" or 5¼" disk), preferably in ASCII format, containing the following analysis information on a particle-by-particle basis:
 - a. Particle number (1, 2, 3...) corresponding to the order in which a particle was analyzed.
 - b. Total x-ray counts acquired for the particle.
 - c. Elemental (Na, Mg, Al, Si...) relative intensity percents calculated by dividing the net counts for each element's spectral region-of-interest by the total x-ray counts and multiplying by 100.
 - d. Average cross-sectional particle diameter (μm).
 - e. Calculated cross-sectional particle area (μm^2).
 - f. Frame number corresponding to the image area that the particle was located in during analysis.
4. Total area imaged (μm^2) per frame on the sample at each magnification.

This information and the five CCSEM analyses must be completed and sent to Mr. Chris Zygarlicke or Mr. Kevin Galbreath of the EERC for processing according to the schedule in Table 21.

5.2.3.4 Task 2: Evaluation and Investigation of the Round-Robin Analysis Results

5.2.3.4.1 Introduction

Data from the test will be compiled and statistically analyzed to provide a measure of the intra- and interlaboratory agreement of CCSEM results. The statistical analysis will provide a quantitative basis for

judging the general performance capability of CCSEM. The compiled data will also be used to investigate possible sources of intra- and interlaboratory variability. After identifying the factors that contribute to the variability, improvements will be made to CCSEM procedures.

5.2.3.4.2 Standardization of CCSEM Data Reduction

Interlaboratory comparison of the analysis results will be hindered because of differences in data reduction routines. Data reduction involves the classification of the particle analyses into various user-specified mineral categories and size intervals. The classification categories are defined based on elemental relative intensities, relative intensity ratios, and stoichiometric criteria. The categories, category definitions, and size intervals are inconsistent among the participating laboratories.

Information supplied by the participating laboratories will be used to develop a standard data reduction/classification routine that will sufficiently characterize the major mineralogy of most coals. Data from each laboratory will be reprocessed with the standard classification routine. By processing the data through a standardized data reduction program, the direct comparison of analysis results will be possible.

5.2.3.4.3 Recommended CCSEM Procedure

A CCSEM procedure will be drafted, based on a thorough review of the initial round-robin analysis parameters and procedures.

5.2.3.5 Task 3: Reporting of CCSEM Round-Robin Test Study

5.2.3.5.1 Information Dissemination

A quarterly newsletter will be sent to participating laboratories. The newsletter will provide current information about the study's progress and will also serve as a forum for participants.

5.2.3.5.2 Report Preparation

A final report will be prepared summarizing the CCSEM round-robin test results and recommendations of the participants. Included in this report will be a detailed description of the recommended procedure and a formal statement regarding the performance characteristics (i.e., repeatability and reproducibility) of the CCSEM method.

5.2.3.6 Proposed Additional Round-Robin Testing

If warranted, an additional round-robin test could be performed to verify the procedure's usefulness and to identify technical weaknesses. This additional test should be conducted according to an internationally acceptable protocol designed following the guidelines of an appropriate professional society (42-44).

5.2.3.7 CCSEM Round-Robin Schedule

The round-robin study of the CCSEM method of coal mineral analysis will proceed according to the schedule in Table 23. The EERC is responsible for

TABLE 23

CCSEM Round-Robin Schedule

Tasks and Subtasks	1992			1993	
	Apr-Jun	Jul-Sep	Oct-Dec	Jan-Mar	Apr-Jun
Task 1: CCSEM Round-Robin Testing
1.1 Sample Distribution	0	0 0 0			
1.2 Acquisition of Test Data	X	X X X			
1.3 Data Compilation			0		
Task 2: Evaluation and Investigation of the Round-Robin Analysis Results
2.1 Statistical Analysis of Test Results			0 0		
2.2 Investigation of Intra- and Interlaboratory Variability			0	0	
2.3 Meeting to Discuss Test Data and Identify Future Directions				X	
2.4 Standardization of CCSEM Data Reduction				X X	X
2.5 Development of a CCSEM Procedure				X X	X
Task 3: Reporting of CCSEM Round-Robin Test Study
3.1 Preparation and Distribution of Quarterly Newsletter		0	0	0	0
3.2 Preparation of Final Report					X X

X = Responsibility of all the round-robin participants.

0 = Responsibility of the Energy & Environmental Research Center.

completing Subtasks 1.1, 1.3, 2.1, 2.2, and 3.1. The involvement of all the round-robin participants is required to complete Subtasks 1.2, 2.3, 2.4, 2.5, and 3.2.

5.3 ZAF Correction of CCSEM Data

A ZAF procedure for the CCSEM routine was made possible by an off-line correction program received from the University of California-Berkeley. This program can be run on a personal computer (PC) in a fraction of the time needed to complete the corrections on-line. The primary reason ZAF corrections were not previously made was because a large amount of time was needed to process the data on the SEM computer. The program requires the k-ratios as measured using integrated counts obtained from the x-ray spectra. The current Particle Recognition and Characterization (PRC) (Tracor Northern) program was modified to produce both the EDS elemental percentages, as before, along with the k-ratios. This requires slightly more time, but is believed to be worth the extra time to retain the capability of comparing data in both forms. The k-ratios are then ZAF-corrected using the PC-based program. This new data format will necessitate modifications to the mineral classification scheme.

To date five ashes and three coals have been used to test the ZAF correction program. The tests were designed to compare the bulk major elemental composition of the coals as determined using both CCSEM with ZAF corrections, and x-ray fluorescence (XRF). X-ray fluorescence is well-established as an ASTM-certified method, and so these data are considered to be reliable as standards for comparison with the new CCSEM-ZAF results. Scanning electron microscope point count (SEMPC) data, when available, are also used for comparison.

CCSEM-ZAF data for five different ash samples were first considered. The samples include two of 100% Wyoming coal ash, and three of ash from a 70/30 blend of Wyoming and Oklahoma coals. For each sample, data obtained using CCSEM-ZAF were compared with XRF and SEMPC results. Bulk compositions, shown in Figure 53 through 57, were measured directly using XRF, and were calculated from particle-by-particle and point-by-point data for the CCSEM-ZAF and SEMPC data, respectively.

Sample #2 of the 100% Wyoming ash (Figure 54) and all three of the blend ash samples (Figures 55 through 57) indicate similar deficiencies for the CCSEM-ZAF data: weight percentages of Fe_2O_3 and CaO are too high and those of MgO , Al_2O_3 , and SiO_2 are too low. The XRF and SEMPC results for the ash samples are in close agreement. The overrepresentation of Fe_2O_3 in the CCSEM-ZAF data sets may be caused by the exceptionally high brightness of Fe-bearing materials in the images used by the SEM (26). MgO , Al_2O_3 , and SiO_2 may be present partially as submicron and organically bound material, and thus not detected using CCSEM. CCSEM-ZAF results for sample #1 of the 100% Wyoming ash (Figure 53) indicate generally opposite trends than those of the other four samples; this particular CCSEM-ZAF analysis may be biased by the inclusion of an unusually high proportion of large particles in the data set.

Three bituminous coals were also used for ZAF testing. CCSEM-ZAF results for Island Creek, Jader, and Kentucky #9 coals were converted to bulk compositions for comparison with XRF data, as shown in Figures 58, 59, and 60.

Figure 53. Bulk composition (SO_3 -free) for 100% Wyoming ash, Sample #1, as determined using XRF, SEMPC, and CCSEM-ZAF.

Figure 54. Bulk composition (SO_3 -free) for 100% Wyoming ash, Sample #2, as determined using XRF, SEMPC, and CCSEM-ZAF.

Figure 55. Bulk composition (SO_3 -free) for Wyoming/Oklahoma blend ash, Sample #1, as determined using XRF, SEMPC, and CCSEM-ZAF.

Figure 56. Bulk composition (SO_3 -free) for Wyoming/Oklahoma blend ash, Sample #2, as determined using XRF, SEMPC, and CCSEM-ZAF.

Figure 57. Bulk composition (SO_3 -free) for Wyoming/Oklahoma blend ash, Sample #3, as determined using XRF, SEMPC, and CCSEM-ZAF.

Figure 58. Bulk compositions (SO_3 -free) for Island Creek coal, as determined using CCSEM-ZAF and XRF.

Figure 59. Bulk compositions (SO₃-free) for Jader coal, as determined using CCSEM-ZAF and XRF.

Figure 60. Bulk compositions (SO₃-free) for Kentucky #9 coal, as determined using CCSEM-ZAF and XRF.

Results are consistent among the three coals, but differ from results for the five ash samples discussed above. For the coals, SiO_2 and K_2O are slightly too high in the CCSEM-ZAF results and too low for Fe_2O_3 . It is not yet clear why the coal and ash samples yielded different trends in the CCSEM-ZAF testing. This issue will be resolved as more analyses are completed as part of ongoing projects. Advances in mass balancing and analysis of submicron particles will be applied to the CCSEM-ZAF results to improve the procedure as more samples are analyzed.

5.4 Particle-by-Particle Scanning Electron Microscopy (PBPSEM)

5.4.1 Introduction

The physical and chemical properties of minerals that control their behavior during coal combustion and ash deposition include size, composition, identity, relative abundance, and degree of association with the organic matrix. Therefore, knowledge of these parameters should facilitate the prediction of mineralogical transformations associated with coal combustion and ash deposition. In recent years, methods employing an automated scanning electron microscope (SEM) have been developed and applied at the EERC for obtaining this important information (20,33). This work has focused primarily on determining the size distribution of minerals in coal and quantifying the mineralogical composition of coal. Currently, our efforts are focused on developing and applying digital image processing and analysis techniques in conjunction with SEM for quantifying the association of mineral grains with the organic coal matrix.

Most SEM digital image processing and analysis systems provide algorithms for acquiring the required morphological data for such an analysis. These algorithms are based on the image segmentation process of transforming an original gray-scale image into a binary image. This process requires operator intervention to select gray-level thresholds for segmenting the coal and mineral phases from the image. Unfortunately, this can be very time consuming and involves subjective judgement by the operator to create binary images that accurately represent the original image. An automatic threshold selection algorithm was formulated and incorporated into an image analysis application program to increase the efficiency of acquiring morphological data and to enhance the objectivity of analysis results (45). The program completely automates digital image acquisition, processing, and image segmentation.

The particle-by-particle scanning electron microscopy (PBPSEM) method, described in this report, integrates this automated SEM image analysis capability with the well-established electron-probe microanalysis technique to measure various morphological and compositional parameters for individual mineral grains in coal. These data are compiled and classified according to compositional criteria into various mineral/chemical categories using a modified version of the Particle Characterization (PARTCHAR) program (20). The program provides a complete statistical summary of the results for all the mineral/chemical phases in a sample, including the proportion of each phase directly associated with coal.

5.4.2 Description of the PBPSEM Method

5.4.2.1 Sample Preparation and Instrumentation

Coals to be analyzed by PBPSEM are pulverized to a standard combustion grind (i.e., approximately 80% of the particles -200 mesh), mounted in carnauba wax (46), cross sectioned, and polished using standard petrographic procedures (47). Samples are then sputter-coated with carbon to minimize electron-beam charging artifacts. A JEOL JSM-35 SEM equipped with a NORAN Instruments (formally Tracor Northern, TN) Micro-Z ultrathin window x-ray detector, TN-5500 x-ray analyzer, TN-5600 stage automation system, TN-8500 image analyzer, and GW Electronics annular solid-state backscattered electron (BSE) detector is utilized for performing PBPSEM analyses.

5.4.2.2 Digital Image Acquisition, Processing, and Analysis

The SEM, operating in the BSE imaging mode, is programmed to analyze preselected areas on the sample. The electron microbeam is rastered across the analysis areas to acquire digital images at a spatial resolution of 512 pixels in both the line-scan (x-) and frame-scan (y-) directions. Frame averaging is employed to enhance image quality.

The PBPSEM routine first acquires a backscattered electron image (BEI). Backscattered electron imaging is used because the production of the backscattered electrons is a function of the average atomic number of the materials under the electron beam. The image produced by the detector will have varying grey scales representing the different chemical compositions in the sample. Areas rich in high atomic number elements will appear much brighter than areas of low average atomic number. Thus in coals, where the average atomic number of the carbonaceous matrix is approximately 6, the mineral phases will be easily identified as their average atomic number is far greater than 6.

A modified version of NORAN Instruments Locked and Liberated image analysis program (48) is used to locate particles and measure various morphological, phase correlation, and compositional parameters. Coal and mineral particles are delineated based on the atomic number contrast inherent in BSE imaging (49). An automatic threshold selection algorithm segments the coal and mineral phases from the gray-scale BSE image into separate binary images (45). The selection algorithm utilizes the image's gray-level histogram. Gray-level histograms of prepared coal samples are generally bimodal consisting of two peaks corresponding to the average brightness (i.e., mean atomic number) of mounting medium and coal, a valley that separates the peaks and represents the less heavily populated intermediate gray levels of coal particle edges, and an essentially featureless region corresponding to a large range in mineral gray-level intensity as a result of compositional variation. In some coal samples, the mounting medium and coal peaks are poorly resolved and the selection algorithm has difficulty in locating the histogram valley separating the two peaks (Figure 61a). A median filter is applied to the image to create a more strongly bimodal histogram (Figure 61b). The filtered histogram facilitates the selection of thresholds by the method described in this section. The median filter was chosen because it suppresses digital image noise without significantly affecting particle edges or other image features (50). The automatic threshold selection algorithm searches for the mounting medium and coal peaks and then selects a threshold at the minimum

Figure 61. Grey-level histograms, (a) original histogram, the selection of thresholds segmenting mounting medium from coal (t_1) and coal from minerals (t_2) is arbitrary; (b) median-filtered histogram (5 x 5 filter), mounting medium and coal peaks are resolved, thus facilitating automatic threshold selection by the method described in the text.

intensity value in the histogram valley (Figure 61b). This method of threshold selection is referred to as the mode method or standard histogram method (51,52). The threshold segments coal from the mounting medium. Another threshold is selected to segment the coal from minerals. The placement of this threshold involves a peak modeling procedure to account for any asymmetry of the coal peak caused by the overlapping of coal and mineral gray levels. The procedure models the coal peak assuming a Gaussian distribution of gray levels and then establishes a threshold at the base of the modeled peak (Figure 61b). Thresholds are determined for each analysis area on the sample to compensate for instrument drift.

After transforming the gray-scale image into coal and mineral phase binaries, the following morphological parameters are determined for each phase of a given particle using standard image analysis routines: minimum, maximum, and average cross-sectional diameter; area; and external perimeter. Two correlation parameters are also determined for each mineral phase: an indication of whether the mineral grain is included, attached, or excluded relative to the coal matrix; and the amount of mineral perimeter in contact with the coal or mounting medium. In addition to this morphological and phase correlation data, compositional information is obtained by acquiring an energy-dispersive x-ray (EDX) spectrum from each mineral grain's center. Spectral regions-of-interest (ROI) are defined to measure the characteristic x-ray emission intensities of twelve common, mineral-forming, major and minor elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, and Ba). Relative intensities are calculated by dividing the net counts for each element by the total ROI counts for all elements. Morphological, phase correlation, and compositional data are collected at three magnifications to provide the spatial resolution necessary to analyze particles ranging widely in size. These data are transferred on-line to a personal computer where it is tabulated and stored to disk for subsequent reduction, report generation, and archival. The acquired BSE images with the locations of EDX analysis are stored to tape.

5.4.2.3 Data Reduction and Reporting

A modified version of the PARTCHAR data reduction program (20) classifies the mineral compositional analyses based on elemental relative intensities, relative-intensity ratios, and stoichiometric criteria into one of 33 mineral/chemical and mineral association categories. Analyses that do not conform to any of the specified criteria are termed unclassified. The program allocates the classified particles according to average diameter into six intervals so that the size distribution of mineral/chemical phases can be determined. A report is generated that summarizes the results in a series of tables containing information on the number, area, and proportions of mineral/chemical phases in their respective size intervals and according to their association with the coal matrix (i.e., included, attached, or excluded). Mineral weight percentages are calculated assuming that particle area is proportional to particle volume (53) and mineral densities are constants.

5.4.3 Future Work

Development of the PBPSEM method is in its infancy and several refinements are required before it can be used routinely for characterizing coal mineralogy. The automatic threshold selection algorithm requires a bimodal gray-level histogram for segmenting the coal particles from mounting medium. This requirement is violated when the area imaged on a sample consists of only coal or mounting medium. Currently, the analysis is performed at low magnifications, generally less than 500 times, to prevent such an occurrence. This practice, however, results in rather poor spatial resolution, thereby limiting the method to analyzing relatively large particles, generally greater than about three microns in average cross-sectional diameter. Other procedures for automatic threshold selection are being investigated to negate this particle-size restriction. Another limitation of the method is the inability to distinguish and quantify mineral-mineral associations for agglomerated particles. This information is

extremely important when considering inorganic transformations that occur during combustion. The threshold selection algorithm currently employed cannot distinguish among various mineral species because of overlapping gray-level intensities. Additional development of the data reduction program is needed to present quantitative mineral-coal association results in formats appropriate for various applications, such as in the field of physical coal cleaning or ash modeling.

Work also needs to be done to optimize and validate the method. The PBPSEM program is currently being tested. Data reduction is in progress; results of these preliminary tests will be discussed in the six-year final report, due in October 1992.

5.4.4 Conclusion

The PBPSEM analysis method has been designed to provide detailed morphological and compositional information on the minerals in coal. Developmental efforts are in progress to optimize the method and assess its performance characteristics (e.g., limitations, repeatability). Work will also continue to extract and quantify the wealth of information provided by this method for various applications.

5.5 Mass Balancing of Inorganic Constituents in Coal

An algorithm to determine the distribution of organically associated inorganics was created using CCSEM, chemical fractionation, and XRF data. The CCSEM data need to be corrected with a ZAF-correction routine that adjusts the data based on atomic number (Z), absorption (A), and fluorescence (F), in order to better represent elemental weight percentages. The CCSEM data are characterized using the PARTCHAR program with a few modifications to allow for the differences between EDS and ZAF corrected numbers. The minerals are then grouped into mineral bins. A physical state and specific gravity are assumed from the mineral type, and the appropriate amount of each oxide is calculated. The major components as well as any impurities are all accumulated as equivalent oxides for each mineral since very few minerals are completely pure.

Data from the three techniques are used to divide the inorganics into soluble minerals, insoluble minerals, organically associated inorganics, and insoluble submicron minerals. The CCSEM data are normalized to the XRF data through a mass balance on silicon. Silicon is assumed to not be present as organically associated and a small amount (5%) is assumed to be submicron. The chemical fractionation and CCSEM data can then be combined on an equivalent oxide basis. The oxides removed during the chemical fractionation technique are either organically associated or soluble minerals. By subtracting out the soluble minerals found in the CCSEM technique, the amount of organically associated constituents can be determined. The amount of submicron inorganics that are insoluble can also be determined by mass balancing the remaining minerals with the XRF and chemical fractionation data. Any submicron minerals which are also soluble during the chemical fractionation technique will be included with the organically associated constituents.

The mass balance was run on the Kentucky #9, Eagle Butte, and Kentucky #9/Eagle Butte blend coals. The results for the three coals are shown in Figures 62, 63, and 64, respectively. These figures show the total

Figure 62. Mass balance results for Kentucky #9 coal.

Figure 63. Mass balance results for Eagle Butte coal.

Figure 64. Mass balance results for Eagle Butte/Kentucky #9 blend coal.

inorganics, mineral inorganics, organically associated inorganics and submicron, insoluble inorganics. The Kentucky #9 shows very little organically associated constituents while the Eagle Butte has a large amount of organically associated calcium and magnesium. The blend lies between the two parent coals. As stated earlier all three coals have an assumed 5% submicron silicon. The submicron silicon is assumed to follow the general trend of the aluminum since they are often together as submicron clay particles. Only the Kentucky #9 coal shows a good correlation between the silicon and aluminum. An iterative balance between the silicon and aluminum would account for this better.

5.6 Analysis of Submicron Particles

5.6.1 Introduction

Scanning electron microscope analysis of coal and ash samples yields size and composition data on a particle-by-particle basis, information that is critical in predicting inorganic transformations during combustion. Through automated techniques, hundreds to thousands of individual particles can be chemically analyzed using energy-dispersive x-ray spectrometry and image processing. A minimum of operator effort is thus required to achieve a statistically significant characterization of the sample.

Electron microscope techniques developed at the EERC have previously been applied to mineral and ash particles with minimum diameters of 1 μm . However, individual-particle analysis is also important for particles with

diameter $<1\ \mu\text{m}$. Submicron particles form during combustion from both organically-associated elements and from minerals in coal.

Most low-rank United States coals contain significant quantities of sodium, magnesium, and calcium, and lesser amounts of potassium, iron, and aluminum, all incorporated into the organic structure of the coal. These organically associated elements commonly vaporize during combustion. Sodium, magnesium, and potassium are particularly volatile and can condense homogeneously as submicron particles if the ratio of vapor phase alkali elements to ash surface area is large. These particles usually react with sulfur dioxide to form submicron sulfate particles by the time they reach the outlet of the boiler.

In contrast to the organically associated elements, mineral particles in coal undergo much less vaporization and condensation during combustion. The degree of vaporization depends on the composition of the local gas. If air is not vigorously mixed with the burning coal particles, reducing zones can exist in the flame. Within the reducing zones, silicon dioxide (SiO_2) in quartz and clays can be reduced to silicon monoxide (SiO), which is volatile. In cooler zones of the furnace, the SiO vapor will oxidize and condense as small SiO_2 particles in much the same way as the vaporized sodium species. However, in most pulverized coal boilers, mixing is rigorous enough that the formation of submicron SiO_2 particles is negligible.

Size reduction of mineral particles can also occur during rapid heating via decomposition or fragmentation. When rapidly heated, pyrite fractures and, upon partial oxidation, forms FeS fragments before melting at 1075°C (53). The extent to which this fragmentation contributes to the formation of submicron particles depends on the degree of mixing of fuel and air; pyrite produces more submicron particles in an oxidizing atmosphere. The carbonate minerals calcite (CaCO_3), siderite (FeCO_3), and ankerite ($\text{CaFe}[\text{CO}_3]_2$) also fragment upon decomposition to form submicron particles (53). In most cases the particle-size distribution of the ash produced during combustion is shifted toward smaller sizes than the size distribution of the coal minerals.

Once formed within the boiler, submicron particles are difficult to remove with particulate control devices. When emitted, these fine particles contribute far more to plume opacity per unit mass than do larger particles (54). The effect of the fine particles on plume opacity is maximized because their size distribution peaks near a diameter equal to the wavelength of visible light, the particle size with the greatest amount of scattering per unit mass (55,56). Understanding of the composition and formation of submicron particles is thus important in mitigating particulate emissions.

Submicron particles are difficult to analyze using automated techniques because their small size places them near the imaging and analytical detection limits of the conventional SEM. Using the recently-acquired ADEM (described above) and a new sample preparation method involving freeze-drying, individual ash particles with diameters as small as $0.1\ \mu\text{m}$ can be analyzed automatically. The new technique is termed scanning electron microscopy with image analysis (SEM-IA), and is generally similar to CCSEM. The sample preparation method, SEM-IA technique, and some applications are described below.

5.6.2 Sample Preparation Method

A new sample preparation method was developed to enable automated SEM analysis of submicron particles. The method involves freeze-drying a small amount of dispersed particles onto a substrate of vitreous carbon. Vitreous carbon is used because its exceptionally smooth surface allows unambiguous identification of small particles. Freeze-drying maintains a uniform separation between particles.

Approximately 10 μg of particulate sample is suspended in 5 mL of purified propanol, to which a drop of dilute organic dispersant has been added. The propanol is first purified by filtration through a 0.05- μm pore polycarbonate filter. The suspension is vibrated ultrasonically for ten minutes to break up any loosely attached particles. Two to five drops of the suspension are placed on a clean piece of vitreous carbon measuring 15x10x3 mm. The sample assemblage is lowered into liquid nitrogen to freeze the particles and propanol into place. After the sample has cooled completely, it is removed from the liquid nitrogen and placed on top of a brass disk measuring approximately 25 mm in diameter and 12 mm in height. The brass disk was previously cooled in liquid nitrogen and serves as a heat sink to prevent overly rapid thawing of the sample. The sample and brass disk are positioned in the bell jar of a vacuum evaporator unit. Thawing under vacuum allows the propanol to evaporate gradually from the sample while preserving a constant spacing between particles. A vacuum of approximately 0.07 Pa is maintained during thawing.

The sample appears dry after approximately 30 minutes, but must remain under vacuum for an additional 60 to 90 minutes to allow its temperature to rise sufficiently to prevent condensation upon removal from the chamber. After removal, samples are coated with a 20-nm thick layer of vacuum-deposited carbon to improve conductivity. The freeze-dried dispersions are suitable for SEM-IA.

5.6.3 Scanning Electron Microscope Analysis of Submicron Particles

The Tracor-Northern ADEM is used for SEM-IA of the freeze-dried sample preparations. A low accelerating voltage (7 kV) is preferred to keep the excitation volume within the particles and to improve imaging. Secondary electron imaging (at 10,000x magnification) and derived binary images are used to locate and measure the size of each particle. The image analysis consists of acquiring 25 digital images of each field of view. The 25 images collected for each field are averaged to remove noise, creating a reference image for that field.

After an average image has been formed, individual ash particles are automatically sized, then analyzed for chemical composition using EDS. Spectra are acquired for 15 seconds at 300 pA. A relatively low-beam current is used to minimize sample damage. Spectra collected using these parameters generally contain sufficient x-ray counts to identify the elemental composition of most submicron particles. The use of a low accelerating voltage results in decreased detection efficiency for many metals, but this does not detract from the analysis of typical sulfate-bearing submicron particles.

A field of view contains approximately 20 individual ash particles. This relatively light particle loading is necessary to prevent electron beam overlap onto adjacent particles during EDS analysis. Each field of view must be manually selected by the operator. Currently, only approximately 200 particles per sample are analyzed because of the operator time required to select each field of view. As SEM-IA analyses become more routine, the number of particles analyzed per sample will increase.

Region-of-interest (ROI) integrated counts and particle-sizing information is saved in the ADEM computer as each field of view is completed. After each sample analysis is complete, the data files are transferred to the Tracor-Northern TN-8500 computer and reduced using the same routines applied to CCSEM data. The classification program PARTCHAR was modified to apply better to submicron particles by including more sulfate types and fewer metal-rich types. Modifications will continue in the future as more samples are characterized.

5.6.4 Tests of the SEM-IA Method

Visual inspection of the freeze-dried sample preparations in the ADEM shows that many individual submicron particles are present. In some instances several submicron particles are fused together to form irregularly shaped aggregates. Such aggregates are common in fly ash and probably form at elevated temperatures prior to emission (57,58). Alternatively, vapor-phase condensation may have occurred following aggregation, smoothing the spherule surfaces together through deposition of coatings. No attempt was made to break up these aggregates, as this would alter the size distribution of the original sample.

Several samples were analyzed to test the SEM-IA method. The analyses were designed to investigate any sampling bias and to compare SEM-IA with CCSEM results for identical samples. Fly ash samples produced from Eagle Butte coal and from a blend of Eagle Butte (70%) and Kentucky #9 (30%) coals were used. Each test is described separately below.

5.6.4.1 Test of Sampling Bias (Eagle Butte)

There was some concern that operator selection of fields of view could result in over representation of the smallest particles. However, large agglomerated groupings of particles are sometimes present in the sample preparation (probably the result of overloading the sample suspension), and so some operator discretion is necessary. A single freeze-dried preparation of Eagle Butte fly ash was analyzed twice using the SEM-IA method: first using fields of view selected because they contained relatively high proportions of submicron particles, then using randomly selected areas.

Size distributions of the two runs are shown in Figure 65. The two runs produced similar results, with both size distributions peaking at particle diameter of $0.4\ \mu\text{m}$. The run emphasizing submicron particles has a second peak at a particle diameter of $25\ \mu\text{m}$, indicating large agglomerates of particles were encountered in the area of the sample preparation used for this run. As mentioned above, these agglomerates are an artifact of the sample preparation procedure. It is not always possible to avoid these agglomerates when choosing fields of view. The agglomerates are easily identified by their

size distribution curve, which is distinctly separate from the curve representing the submicron particles (Figure 65) and can easily be removed from the data set after the analysis is completed.

The results of these two runs suggest that the true size distribution of the sample is accurately measured by the SEM-IA method. The peak at diameter $0.4\ \mu\text{m}$ may indicate a uniformity of ash formation processes leading to a consistent particle size.

5.6.4.2 Comparison of SEM-IA and CCSEM Methods (Eagle Butte)

In order to directly compare SEM-IA and CCSEM results, the same freeze-dried dispersion of Eagle Butte fly ash was analyzed using both SEM-IA and CCSEM. In addition, a standard dispersion of the same ash sample was prepared and analyzed using CCSEM. Results are shown in Table 24. Particle compositions for the SEM-IA and CCSEM analyses are completely different, whereas the results for the two CCSEM runs are similar. Particles detected using SEM-IA are predominantly sulfate-, phosphate-, and chloride-rich, whereas those detected through CCSEM represent an assortment of minerals, mostly Ca-rich, including Ca aluminate, Ca-silicate, gypsum/Al-silicate, Ca-Al-silicate, and others. A minor amount of sulfate-rich particles are also present in the CCSEM data sets.

Figure 65. Size distributions for SEM-IA results for Eagle Butte parent ash, using a freeze-dried sample preparation.

The compositional variations between the SEM-IA and CCSEM data sets reflect the different size ranges represented by the two types of analyses. In the SEM-IA run, the maximum particle diameter in Table 24 was 1.6 μm . Large agglomerates, with diameters of 25 μm and greater, are sample preparation artifacts and were not included in the table. The CCSEM analyses include only particles with diameters $>1 \mu\text{m}$, and so most of the particles detected using SEM-IA would not be included in the CCSEM results.

It is less clear why the SEM-IA results do not include many particles with diameters in the low end of the CCSEM range, i.e., those with diameters of 2 to 10 μm . Apparently the fields of view selected for SEM-IA analysis contained few or no particles in this size range, in contrast to the areas used for CCSEM. Only a very small area of the sample was used to obtain data for 226 particles through SEM-IA. The CCSEM analysis of the same freeze-dried preparation included a much larger area (at lower magnification), yielding data for 453 particles. The CCSEM analysis of the standard dispersion

Table 24
Results of SEM-IA and CCSEM Analyses
Mineral weight percentages for Eagle Butte Fly Ash

Mineral	SEM-IA run (freeze-dry)	CCSEM run (freeze-dry)	CCSEM run (standard)
Quartz	0	3.8	6.5
Iron Oxide	0	1.6	0.2
Periclase	1.6	0	0
Alumina	0	0.3	0
Calcite	0	0.7	0.8
Dolomite	0	3.0	5.0
Kaolinite	0	1.5	0
Ca Al-Silicate	0	5.0	6.2
Na Al-Silicate	0	4.3	2.3
Mixed Al-Silicate	0	1.6	1.1
Ca-Silicate	0	6.5	2.6
Ca Aluminate	0	17.3	24.4
Sulfate-Rich	42.7	2.0	1.3
Phosphate-Rich	16.2	0	0
Chloride-Rich	11.4	0	0
Gypsum/Al-Silicate	0	5.8	2.8
Si-Rich	0	0.6	1.6
Ca-Rich	0	5.9	2.9
Ca-Si-Rich	0	2.2	2.6
Unknown	28.1	37.7	39.9
TOTALS	100.0	100.0	100.0

included 1013 particles. In the future, SEM-IA runs will be lengthened to make them more directly comparable with CCSEM analyses. The similarity between the results for the two CCSEM runs indicate that the freeze-dried preparation yields results similar to those of the standard dispersion.

The distinct compositional variation between the submicron size fraction (as measured using SEM-IA) and the supermicron fraction (measured using CCSEM) confirms that they are formed through different processes. Condensation of alkali vapors is evidently the primary mechanism for formation of submicron particles, while the mineral-rich content of the supermicron particles indicates they probably formed through decomposition and fragmentation.

5.6.4.3 Comparison of SEM-IA and CCSEM Methods (Eagle Butte/Kentucky #9 Blend)

The SEM-IA method was also evaluated by comparison with CCSEM results for ash from the Eagle Butte/Kentucky #9 70/30 blend. In this case, a freeze-dried dispersion was analyzed using SEM-IA, and a standard dispersion prepared from the same sample was analyzed using CCSEM (Table 25). As for the Eagle Butte ash samples discussed above, the results for the blend ash show distinct size-related compositional variations. The SEM-IA results, which include data for particles with a maximum diameter of 1.6 μm only, are dominated by sulfates, phosphates, and chlorides. No typical coal minerals were identified in the SEM-IA data set. Almost half of the particles identified using SEM-IA were classified as "unknown"; these may represent coated mineral particles or others of mixed composition.

The CCSEM data for the blend ash indicate a range of minerals. As for the Eagle Butte ash, the mass of the blend ash analyzed using CCSEM is concentrated in particles with diameters from 1 to 10 μm . The CCSEM results for the blend ash indicate more sulfate-rich particles and fewer Ca-bearing particles than the results for the Eagle Butte ash.

5.6.5 Conclusions

SEM-IA and CCSEM results for the Eagle Butte ash and the Eagle Butte/Kentucky #9 blend ash clearly indicate a size-related shift in composition, from mineral-rich particles in the supermicron fraction, to sulfate-, phosphate-, and chloride-rich particles in the submicron fraction. As more SEM-IA results are obtained, the particle classification scheme will be further refined to better identify coated and mixed particles currently grouped into the "unknown" category. Future SEM-IA analyses will include areas of the samples, in order to obtain data for a sufficient number of supermicron particles, for better comparison with CCSEM results. The results presented above show SEM-IA to be a promising technique for characterization of submicron particles. The unique compositions of particles in the submicron size fraction suggest that individual-particle analysis of these smallest particles is essential to achieving an overall understanding of the transformations occurring during combustion.

Table 25

Results of SEM-IA and CCSEM Analyses
Mineral Weight Percentages for Eagle Butte/Kentucky #9 Blend Ash

Mineral	SEM-IA (freeze-dry)	CCSEM (standard)
Quartz	0	6.5
Iron oxide	0	0.5
Rutile	0	0.1
Alumina	0	0.1
Calcite	0	1.4
Ankerite	0	0.2
Kaolinite	0	6.3
Montmorillonite	0	1.8
K Al-silicate	0	0.5
Fe Al-silicate	0	3.9
Ca Al-silicate	0	9.2
Na Al-silicate	0	9.7
Aluminosilicate	0	0.1
Mixed Al-silicate	0	2.4
Ca silicate	0	1.9
Ca aluminate	0	1.4
Sulfate-rich	24.5	17.7
Phosphate-rich	13.4	0
Chloride-rich	14.7	0
Gypsum/Al-silicate	0	3.0
Si-rich	0	3.0
Ca-rich	0	0.1
Ca-Si-rich	0	0.6
Unknown	47.4	29.4
Totals	100.0	100.0

6.0 CONCLUSIONS

6.1 Task 1

Work on ASHPERT has included the development of algorithms for predicting ash particle-size distribution (PSD) and mineral frequency distribution (MFD) from the corresponding parent coals' PSDs and MFD. The database for this expert system currently contains the proximate/ultimate, XRF, chemical fractionation, and CCSEM data for 45 samples. In addition, the database also contains the sample's name, rank, location, biography, and ownership category. Routines to manage and analyze the database were also developed. To date, four different topologies and two different transformation models have been implemented and tested. The MARS topology with the linear transformation model emerges as the best "rule" for endowing

ASHPERT with the requisite expertise. The MARS topology "predicted" values are, on average, in error by about 8%. It is interesting to observe that the entire ASHPERT database of over 15 megabytes has been defined by a linear operator (a matrix in this case) requiring only about 5 kilobytes.

As to future directions for ASHPERT, a rigorous justification of the continuity hypothesis needs to be undertaken. Additional transformation models, especially nonlinear ones, need to be tested, since this may permit better correlations to be established with a smaller basis set than the currently used set of mineral types. The replacement of the linear operator by a neural network is very viable and would be a significant improvement. Additional analyses of the database need to be performed to extract possible parameters for the deterministic and stochastic classes of models. Such models need to be incorporated as part of ASHPERT's knowledge base, which will then allow ASHPERT to approximate fly ash distributions at various "stages" or locations within a combustor. Finally, additional work on the theoretical aspects of particle size and composition distribution (PSCD) evolution is also needed to improve our understanding of the physical and chemical processes involved in this complex transformation.

A mechanistic model for fly ash composition and size prediction was also devised. This model, ATRAN1, employs stochastic principles of mathematical random-combining of coal inorganic constituents to form the predicted fly ash. An algorithm has been formulated so that organically bound inorganic constituents are included in the program. Three coals were tested using the predictive model: Eagle Butte, Kentucky #9, and a blend of Kentucky #9 (30%) and Eagle Butte (70%). Preliminary results revealed that the Eagle Butte contained a larger amount of nucleated submicron particles due to the large amount of organically associated constituents present in the coal. Experimental fly ash produced using particle residence times and temperatures associated with fouling conditions in a boiler have not yet been generated on the coals in order to compare experimental and predicted fly ash composition and size. However, experimental fly ash was generated under slagging conditions (shorter particle residence times than fouling conditions) for the blend. The CCSEM mineral/phase composition of the experimental blend fly ash compared fairly well with that of the predicted blend composition, the only variances being with the complex aluminosilicates. Particle-size distributions also compared fairly well between the experimental and predicted blends.

6.2 Task 2

The tests performed on synthetic coal model mixtures were completed. Reaction kinetics determinations revealed that the state of Ca (organic or inorganic) in the Ca-Si-S system had a significant effect on the combustion of the synthetic chars. Detailed characterization of the Ca(min.)-S-Si system was performed to elucidate interactions between calcium, silica, and sulfur. Extensive surface condensation of CaO and calcium sulfate was observed at gas temperatures of 1300°C or lower. The formation of calcium silicate was most extensive at 1500°C. Fly ash particle sizes were larger at 900° and 1100°C than at 1300° and 1500°C, possibly because of more sticky calcium sulfate-silicate glue available at the lower temperatures. Char and calcite fragmentation was evident when combusting the Ca(min.)-Si-S mixture at 1500°C. The Fe(min.)-Al-Si system loses nearly all the sulfur from the pyrite at 900°C, leaving kaolinite and iron oxide. The system shows only a small degree

of interaction between the kaolinite and iron until 1500°C, when an increased amount of iron aluminosilicate components form.

A blend of 70% Wyoming Eagle Butte low-sulfur (<1% mf) subbituminous coal and 30% Kentucky #9 high-sulfur (4% mf) bituminous coal was analyzed using CCSEM. Experimental fly ash was generated in the DTF under slagging conditions, using a gas temperature of 1500°C and residence time of about 2.5 seconds. Ash was also produced under fouling conditions, using an extended residence time and lower temperatures. The fly ash was analyzed using SEMPC and CCSEM. Coal analyses revealed that the blending operation was quite successful as the physical and chemical components are nearly weighted averages of the components in the parent coals. The fly ash revealed very little interaction between the mineral components of the two different coals. Viscosity distributions of liquid phases in the fly ash under slagging conditions, for the experimental ash and a weighted average of the parent fly ashes, were similar. Iron-rich particles derived from the pyrite in the Kentucky #9 coal experienced only limited interaction with aluminosilicates, most of which had sources in the Kentucky #9.

6.3 Task 3

A round-robin CCSEM analysis has been initiated which involves seven laboratories, including UNDEERC, Ames Laboratory-Iowa State University, Sandia National Laboratory, the University of Kentucky, the R.J. Lee Group, the Netherlands Energy Research Center, and CSIRO of Australia. Three Argonne National Laboratory premium coals including Illinois #6, Pittsburgh #8, and Wyodak were prepared by CSIRO for potential analysis. Information was gathered from each of the participating laboratories regarding their CCSEM system and used to prepare a standard format for how the participants should configure their SEM system to analyze the coals. The results of the preliminary round-robin testing will be used to design further testing and refinement of the CCSEM technique, possibly leading to eventual certification of the method by an appropriate professional society.

A correction for improving the accuracy of CCSEM elemental compositions was devised. This procedure involves the extraction of k-ratios during acquisition of CCSEM data, followed by correction of these k-ratios for atomic number (Z), absorption (A), and fluorescence (F) effects. This ZAF correction results in more accurate quantitative chemistries of individual fly ash particles or minerals. Five ash samples and three coals were analyzed to test the CCSEM-ZAF technique. Bulk composition of these ashes and coals were calculated from the CCSEM-ZAF data and compared to bulk compositions derived from XRF and SEMPC analyses. Results indicate a reasonable correspondence between the techniques, with the exception of elements commonly concentrated in the organic matrix and/or the submicron particulate size fraction.

A semiautomated PBPSEM analysis technique was devised and refined into a fully automated technique. This new technique uses advanced image analysis along with the standard CCSEM procedure to give the size and composition of coal minerals on an individual coal-particle basis. This technique greatly enhances ash formation and deposition models by providing much more comprehensive coal input data. The major operating parameter affecting the sizing and location of particles is the determination of the difference between coal and minerals in the gray-level histogram. The method now used to determine this difference works well for completely homogeneous systems.

Present efforts are focused on determining the reproducibility of gray-level histograms in heterogeneous coal systems and developing ways of improving the distinction between the different components in the system. Samples are currently being tested to determine the accuracy of the PBPSEM technique.

A method has been devised to mass balance organically and mineralogically associated inorganics in coal so that their sum equals the total ash content of the coal. An algorithm to determine the distribution of organically associated inorganics was created using computer controlled scanning electron microscopy (CCSEM), chemical fractionation, and x-ray fluorescence (XRF) data. Data from the three techniques are used to divide the inorganics into soluble minerals, insoluble minerals, organically associated inorganics, and insoluble submicron minerals. The mass balancing technique was tested on the Kentucky #9, Eagle Butte, and Kentucky #9/Eagle Butte blend coals. Kentucky #9 coal contained very little organically associated constituents, whereas the Eagle Butte coal had a large amount of organically associated calcium and magnesium. The organically bound content for the Kentucky #9/Eagle Butte blend was intermediate between the two parent coals.

A new method for automated analysis of individual submicron particles has been developed. Scanning electron microscopy with image analysis (SEM-IA) is similar to the CCSEM method for larger particles, but uses the Tracor-Northern ADEM to enable analysis of particles as small as 0.1 μm in diameter. Preliminary results show the submicron fractions of ash samples to have an entirely different composition from that of the larger particles. The submicron size fraction typically contains sulfates, phosphates, chlorides, and mixed particles, compared with the aluminosilicates and Ca-rich particles found in the supermicron fractions. The distinct compositions of the two size fractions confirm that they form through different processes, probably primarily fragmentation and coalescence for the supermicron particles, and vaporization and condensation for the submicron particles.

7.0 REFERENCES

1. Zygarlicke, C.J.; McCollor, D.P.; Toman, D.L.; Erickson, T.A.; Ramanathan, M.; Folkedahl, B.S. "Combustion Inorganic Transformations," Semiannual Technical Progress Report for the Period July 1, 1991 - December 31, 1991. USDOE Cooperative Agreement No. DE-FC21-86MC10637, 1992.
2. Benson, S.A.; Holm, P.L. "Comparison of Inorganic Constituents in Three Low-Rank Coals," *Ind. Eng. Chem. Prod. Res. Dev.* 1985, 24, 145.
3. Kalmanovitch, D.P.; Montgomery, G.G.; Steadman, E.N. "Computer-Controlled Scanning Electron Microscope Characterization of Coal Ash Deposits," ASME Paper Number 87-JPGC-FACT-4, 1987.
4. Dunn-Rankin, D. "Kinetic Model for Simulating the Evolution of Particle Size Distribution During Char Combustion," *Combust. Sci. and Tech.* 1988, 58, 297-314.

5. Huang, J.; Edwards, B.F.; Levine, A.D. "General Solutions and Scaling Violations for Fragmentation With Mass Loss," Department of Physics, West Virginia University, 1991, preprint.
6. Baxter, L.L.; Abbot, M.F.; Douglas, R.E. "Dependence of Elemental Ash Deposit Composition on Coal Ash Chemistry and Combustor Environment," 1991, preprint.
7. Cai, M.; Edwards, B.F.; Han, H. "Exact and Asymptotic Scaling Solutions for Fragmentation with Mass Loss," *Phys. Rev.* **1991**, *A* (43), 656-662.
8. Beer, J.M.; Sarofim, A.F.; Barta, L.E. "From Coal Mineral properties to Fly Ash Deposition Tendencies: A Modelling Route," *J. Inst. Energy* **1992**, *65*, 55-62.
9. Kerstein, A. R.; Edwards, B.F. "Percolation Model for Simulation of Char Oxidation and Fragmentation with Time-Histories," *Chem. Eng. Sci.* **1987**, *42*, 1629-1634.
10. Edwards, B. F.; Ghosal, G.K. "Model of Ash Size Distributions from Coal Char Oxidation," Department of Physics, West Virginia University, 1991, preprint.
11. Ullman, J.D. "Principles of Database and Knowledge-Based Systems, Vol. I: Classical Database Systems," Comp. Sci. Press: Maryland, 1988.
12. Goldstein, J. I.; Newbury, D.E.; Echlin, P.; Joy, D.C.; Fiori, C; Lifshin, E. "Scanning Electron Microscopy and X-Ray Microanalysis," Plenum Press: ew York, 1981.
13. Dinger, D. R. "New Stereological Method for Obtaining 3-Dimensional Grain Size Distributions and Shape Factors from Planar Sections: Application to Characterization of Mineral Matter in Coal," Ph.D. Thesis, Pennsylvania State University, 1975.
14. DeHoff, R. T.; Rhines, F.N. "Quantitative Microscopy," McGraw-Hill: ew York, 1968.
15. Ramanathan, M. "Particle Size and Composition Distribution in Coal Combustion Systems: Phenomenology and Expertise," *In Proceedings of the Expert System Applications for the Electric Power Industry*, Boston, MA, September 9-11, 1991.
16. Senior, C.L. "Submicron Aerosol Production During Combustion of Pulverized Coal," Ph.D. Thesis, California Institute of Technology, 1984.
17. Erickson, T.A. "The Fate of Flame Volatilized Sodium during the Combustion of Pulverized Coal in Reaction with Silica and Sulfur (Studied with the Aid of a Synthetic Coal)," Masters Thesis, University of North Dakota, 1990.
18. Ludlow, D.K.; Erickson, T.A.; Benson, S.A. *Energy and Fuels* **1991**, *5*, 539.

19. Zygarlicke, C.J.; Toman, D.L.; Erickson, R.A.; Ramanathan, M.; Folkedahl, B.C. "Combustion Inorganic Transformations," Final Technical Progress Report for the Period July 1, 1990 - June 30, 1991, USDOE Contract No. DE-FC21-86MC10637, University of North Dakota Energy and Environmental Research Center, Grand Forks, ND, 1991.
20. Zygarlicke, C.J.; Steadman, E.N. "Advanced SEM Techniques to Characterize Coal Minerals," *Scanning Microsc. Int.* 1990, 4 (3), 579.
21. McCollor, D.P.; Jones, M.L.; Benson, S.A.; Young, B.C. 22nd International Symposium on Combustion, The Combustion Institute, Pittsburgh, 1988, p 59.
22. Kalmanovitch, D.P.; Frank, M. "An Effective Model of Viscosity for Ash Deposition Phenomena," Presented at the Conference on Mineral Matter and Ash Deposition from Coal, The Engineering Foundation, Santa Barbara, CA, February 21-26, 1988.
23. Vorres, K.S. *Users Handbook for the Argonne Premium Coal Sample Program*; Argonne National Laboratory, 1989, 64 p.
24. Vorres, K.S. "The Argonne Premium Coal Sample Program," *Energy & Fuels* 1990, 4 (5), 420-426.
25. Lee, R.J.; Kelly, J.F. "Overview of SEM-Based Automated Image Analysis," *Scanning Electron Microscopy* 1980, 1, 303-310.
26. Huggins, F.E.; Kosmack, D.A.; Huffman, G.P.; Lee, R.J. "Coal Mineralogies by SEM Automatic Image Analysis," *Scanning Electron Microscopy* 1980, 1, 531-540.
27. Huggins, F.E.; Huffman, G.P.; Lee, R.J. "Scanning Electron Microscope-Based Automated Image Analysis (SEM-AIA) and Mössbauer Spectroscopy: Quantitative Characterization of Coal Minerals," In *Coal and Coal Products: Analytical Characterization Techniques*; Fuller, E.L. Jr., Ed.; American Chemical Society Symposium Series 205, 1982, Chapter 12, p. 239-258.
28. Straszheim, W.E.; Markuszewski, R. "Automated Image Analysis of Minerals and Their Association with Organic Components in Bituminous Coals," *Energy & Fuels* 1990, 4 (6), 748-754.
29. Straszheim, W.E.; Markuszewski, R. "Engineering Insights from Automated Image Analysis of Mineral Matter in Coal," In *Mineral Matter and Ash Deposition from Coal*; Bryers, R.W.; Vorres, K.S., Eds.; Engineering Foundation: New York, 1990, pp 53-61.
30. Straszheim, W.E.; Markuszewski, R. "Automated Image Analysis of the Association of Ash-Forming Mineral Matter with Coal Particles," *Prepr. Pap.--Am. Chem. Soc., Div. Fuel Chem.* 1991, 36 (1), 216-222.

31. Straszheim, W.E.; Yousling, J.G.; Younkin, K.A.; Markuszewski, R. "Mineralogical Characterization of Lower-Rank Coals by SEM-Based Automated Image Analysis and Energy Dispersive X-Ray Spectrometry," *Fuel* 1988, 67, 1042-1047.
32. Zygarlicke, C.J.; Steadman, E.N.; Benson, S.A. "Studies of Transformations of Inorganic Constituents in a Texas Lignite During Combustion," *Prog. Energy Combust. Sci.* 1990, 16, 195-204.
33. Jones, M.L.; Kalmanovitch, D.P.; Steadman, E.N.; Zygarlicke, C.J.; Benson, S.A. "Application of SEM Techniques to the Characterization of Coal and Coal Ash Products," In *Advances in Coal Spectroscopy*; Meuzelaar, M.L.C., Ed.; Plenum Publishing Corp.: New York, 1992; Chapter 1, pp 1-27.
34. Casuccio, G.S.; Gruelich, F.A.; Hamburg, G.; Huggins, F.E.; Nissen, D.A.; Vleeskens, J.M. "Coal Mineral Analysis: A Check on Interlaboratory Agreement," *Scanning Microscopy* 1990, 4 (2), 227-236.
35. Vleeskens, J.M.; Hamburg, G. "Coal Minerals Analysis 'Round Robin,' Data Compilation," *Stichting Energieonderzoek Centrum Nederland*, ECN-89-154 (December 1987, updated October 1989), unpublished ECN internal report, 25 p.
36. Birk, D. "Coal Minerals: Quantitative and Descriptive SEM-EDX Analysis," *Journal of Coal Quality* 1989, 8 (2), 55-62.
37. Hamburg, G. "Description of the Tracor Northern Energy Dispersive System as Applied to Coal Minerals Analysis," *Technology in Review* 1984, 2 (1), 7-10.
38. Doughten, M.W.; Gillison, J.R. "Determination of Selected Elements in Whole Coal and in Coal Ash from the Eight Argonne Premium Coal Samples by Atomic Absorption Spectrometry, Atomic Emission Spectrometry, and Ion-Selective Electrode," *Energy & Fuels* 1990, 4 (5), 426-430.
39. Palmer, C.A. "Determination of Twenty-Nine Elements in Eight Argonne Premium Coal Samples by Instrumental Neutron Activation Analysis," *Energy & Fuels* 1990, 4 (5), 436-439.
40. Evans, J.R.; Sellers, G.A.; Johnson, R.G.; Vivit, D.V.; Kent, J. "Analysis of Eight Argonne Premium Coal Samples by X-Ray Fluorescence Spectrometry," *Energy & Fuels* 1990, 4 (5), 440-442.
41. Wertz, D.L. "X-Ray Analysis of the Argonne Premium Coals: 1. Use of Absorption/Diffraction Methods," *Energy & Fuels* 1990, 4 (5), 442-447.
42. American Society for Testing and Materials. "Practice for Conducting an Interlaboratory Study to Determine the Precision of Test Methods (E691)," *Annual Book of ASTM Standards* 1992, 14.02.
43. Association of Official Analytical Chemists. "AOAC Guidelines for Collaborative Study Procedure to Validate Characteristics of a Method of Analysis," *Journal of the Association of Official Analytical Chemists* 1988, 71, 161.

44. Horwitz, W. "Protocol for the Design, Conduct, and Interpretation of Collaborative Studies," *Pure and Applied Chemistry* 1988, 60 (6), 855-864.
45. Galbreath, K.C., Brekke, D.W., and Folkedahl, B.C. "Automated Analytical Scanning Electron Microscopy and Image Analysis Methods for Characterizing the Inorganic Phases in Coal and Coal Combustion Products," *ACS Fuel Chem. Division Preprints* 1992, 37 (in press).
46. Straszheim, W.E.; Younkin, K.A.; Greer, R.T.; Markuszewski, R. "Mounting Materials for SEM-Based Automated Image Analysis of Coals," *Scanning Microscopy* 1988, 2 (3), 1257-1264.
47. American Society for Testing and Materials (ASTM). "Standard Practice for Preparing Coal Samples for Microscopical Analysis by Reflected Light (D2797)," *Annual Book of ASTM Standards* 1991, 5.05, 308-311.
48. Wagner, A.M.; Pekowsky, B.C. "Locked and Liberated Analysis," *Tracor Northern Advanced Imaging Applications* 1989, Tracor Northern, Middleton, Wisconsin, p 4.
49. Lloyd, G.E. "Atomic Number and Crystallographic Contrast Images with the SEM: A Review of Backscattered Electron Techniques," *Mineralogical Magazine* 1987, 51, 3-19.
50. Twogood, R.E.; Sommer, F.G. "Digital Image Processing," *IEEE Transactions on Nuclear Science* 1982, NS-29 (3), 1076-1086.
51. Weszka, J.S. "A Survey of Threshold Selection Techniques," *Computer Graphics and Image Processing* 1978, 7, 259-265.
52. Kohler, R. "A Segmentation System Based on Thresholding," *Computer Graphics and Image Processing* 1981, 15, 319-338.
53. Raask, E. "Mineral Impurities in Coal Combustion," New York: Hemisphere Publishing Corp., 1984.
54. Balfour, D.A.; Meserole, F.M.; Defries, T. "Utility Stack Opacity Troubleshooting Guidelines," Final report, EPRI Research Project No. 2250-3, 1991.
55. Mie, G. "Beitrage zur Optik truber Medien speziell kolloidaler Metallosungen," *Ann. Phys.* 1908, 25, 377-445.
56. Bohren, C.F.; Huffman, D.R. "Absorption and Scattering of Light by Small Particles," New York: John Wiley & Sons: 1983, 530 p.
57. Hazrati, A.; Schrod, J.T. "Microcharacterization of Micron/Submicron Fly Ash from a Pulverized-Dry-Coal-Burning Power Plant," *Surf. Interface Anal.* 1988, 13, 142-148.
58. Kaufherr, N.; Lichtman, D. "Comparison of Micron and Submicron Fly Ash Particles Using Scanning Electron Microscopy and X-Ray Elemental Analysis," *Environ. Sci. Technol.* 1984, 18 (7), 544-547.

APPENDIX A

SUMMARY OF ORGANICALLY BOUND CONSTITUENTS IN PARENT COALS AND BLEND

SUMMARY OF ORGANICALLY BOUND CONSTITUENTS IN PARENT COALS AND BLEND
(wt% Coal Basis)

Eagle Butte

	Initial (ppm)	Removed by H ₂ O (%)	Removed by NH ₄ OAc (%)	Removed by HCl (%)	Remaining (%)
Silicon	7,325	0	0	0	100
Aluminum	4,889	0	11	35	54
Iron	2,770	2	0	68	30
Titanium	580	0	17	0	83
Phosphorus	215	0	34	57	9
Calcium	12,084	0	70	30	0
Magnesium	3,552	0	85	12	3
Sodium	573	16	78	2	4
Potassium	85	0	41	0	59

Kentucky #9

	Initial (ppm)	Removed by H ₂ O (%)	Removed by NH ₄ OAc (%)	Removed by HCl (%)	Remaining (%)
Silicon	28,526	0	0	0	100
Aluminum	14,401	0	0	3	97
Iron	24,625	14	0	6	80
Titanium	538	0	0	0	100
Phosphorus	129	6	51	43	0
Calcium	7,227	34	59	1	6
Magnesium	990	3	16	14	68
Sodium	739	30	33	2	35
Potassium	2,503	2	6	4	88

70/30 Blend

	Initial (ppm)	Removed by H ₂ O (%)	Removed by NH ₄ OAc (%)	Removed by HCl (%)	Remaining (%)
Silicon	16,109	0	0	0	100
Aluminum	8,416	0	0	22	78
Iron	10,753	20	0	20	60
Titanium	561	0	0	0	100
Phosphorus	227	0	35	60	6
Calcium	10,481	5	66	26	3
Magnesium	2,819	8	74	9	9
Sodium	747	47	33	3	16
Potassium	711	0	0	0	100

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Combustion Inorganic Transformations (3.2)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-86
		6. Completion Date 9-30-92

7. FY 91/92	8. Months or Quarters Quarters	1991 JUL AUG SEP OCT NOV DEC	1992 JAN FEB MAR APR MAY JUN
9. Cost Status	a. Dollars Expressed in Thousands	b. Dollar Scale	
10. Cost Chart			
Fund Source		c. Cumulative Accrued Costs	
DOE		Planned	
P		92	
A		95	
P		80	
A		75	
P		92	
A		89	
P		91	
A		366	
P		319	
A		366	
Total P		366	
Total A		319	
Variance		47	
P = Planned A = Actual		Actual	
Total Planned Costs for Program/Project		92	
\$366		183	
		275	
		366	
		319	
		47	

11. Major Milestone Status	Units Planned	
	Units Complete	
1. Fly Ash Particle-Size and Composition Prediction	P	a v b v c v d e v f v g A
	C	
	P	
	C	
2. Laboratory-Scale Combustion Testing	P	a v b v c d e v f v g A
	C	
	P	
	C	
3. Analytical Methods Development	P	a v d v f v c v g v e v b h A
	C	
	P	
	C	
4. Collaborative Research	P	a A
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks
Due to the EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date	14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

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4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task 1	Fly Ash Particle-Size and Composition Prediction:				
1.a	Production of experimental fly ash for Eagle Butte, Beulah, and Eagle Butte/Kentucky #9 blend coals.	7-31-91	7-31-91		
1.b	Addition of coal mineral and corresponding drop-tube furnace fly ash data from a low-rank and a high-rank coal to the ASHPERT model.	10-31-91	10-31-91		
1.c	Testing of stochastic model on Eagle Butte, Beulah, and Eagle Butte/Kentucky #9 blend. Stochastic model refinement and assessment of strengths and weaknesses.	11-15-91	11-15-91		
1.d	Refinement of the ASHPERT model to include organically bound inorganics in the prediction process.	11-30-91	11-30-91		
1.e	Expansion of the ASHPERT knowledge base to 40 coals and fly ashes.	3-31-92	3-31-92		
1.f	Testing of the ASHPERT model on four coals.	5-31-92			
1.g	Compilation of a document explaining the contents of the ASHPERT data base and the expert-system process.	6-15-92			
Task 2	Laboratory-Scale Combustion Testing:				
2.a	Formulate a synthetic coal/char model mixture with included inorganics consisting of pyrite and aluminosilicate.	8-31-91	8-31-91		
2.b	Characterize char and fly ash from the Eagle Butte/Kentucky #9 blend and evaluate mineral coalescence and fragmentation phenomena.	11-15-91	11-15-91		
2.c	Determination of char reactivity by calculating reaction kinetics during the combustion of Eagle Butte, Beulah, and Eagle Butte/Kentucky #9 blend coals.	12-31-91	12-31-91		
2.d	Combustion testing of the pyrite-aluminosilicate model mixture to note inorganic transformations and pyrite fragmentation.	1-31-92	12-31-91		
2.e	Mineral transformations under fuel-rich conditions in the drop-tube furnace.	3-15-92	3-15-92		

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FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

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4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
2.f	Consideration activity report for conducting future drop-tube furnace studies in ash deposition.	5-31-92			
2.g	Comparison of drop-tube furnace fly ash properties with those generated at the pilot or full scale.	6-15-92			
Task 3	Analytical Methods Development:				
3.a	The ZAF correction procedure for CCSEM chemistries will be tested, and the computer program for its use will be made user friendly.	10-31-91	10-31-91		
3.b	Results of the first round of samples being analyzed by the round-robin participants will be compiled.	6-15-92			
3.c	The particle-by-particle SEM (PBPSEM) method for coal analysis will be completed.	4-15-92			
3.d	Develop SEM technique to analyze coal minerals or ash particles that are less than 5 μ m.	1-31-92	1-31-92		
3.e	Round-robin results will be reported, and suggestions will be made for standardization of the CCSEM technique.	2-29-92			
3.f	Investigation of mass-balancing inorganics in low-rank coal using chemical fractionation and CCSEM.	3-31-92	3-31-92		
3.g	Testing of the PBPSEM method will be performed on previously analyzed coals.	5-31-92			
3.h	Meeting(s) will be held with ASTM officials for guidance in the ASTM standardization process.	6-30-92			
Task 4	Collaborative Research:				
4.a	Collaborative research with PSIT will continue during the third year of the CIT project.	2-15-92	2-15-92		

3.4 Liquefaction Reactivity of Low-Rank Coals

LIQUEFACTION REACTIVITY OF LOW-RANK COALS

**Semiannual Technical Progress Report
for the Period January - June 1992**

by

**Edwin S. Olson, Research Supervisor
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for

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Pittsburgh Energy Technology Center
626 Cochran Mill Road
Pittsburgh, PA 15236**

July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

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LIQUEFACTION REACTIVITY OF LOW-RANK COALS

1.0 EXECUTIVE SUMMARY

Coal liquefaction has been effectively carried out in a number of laboratories with carbon monoxide reductant in an aqueous solvent (CO steam process). Catalysts are sought which could improve the conversion in the process and avoid the high pressures required. Australian workers demonstrated that sodium aluminate is able to catalyze the conversion of Australian coals in the CO/water system and in water/hydrogen donor solvent mixtures. The Energy and Environmental Research Center (EERC) project has focused on demonstrating an economical process for the liquefaction of low-rank coal, and aqueous sodium aluminate has been utilized as the catalyst. High conversions comparable with those obtained with hydrogen donor solvents and hydrogen sulfide were obtained. The product consists of a large distillate fraction composed of oxygenated compounds and many aromatics. The asphaltene and oil fractions are suitable for second-stage catalytic hydrogenation. Reactions utilizing hydrogen as the reductant gave low conversions with sodium aluminate.

The use of a mixed solvent system for the CO reduction was investigated. A solvent composed of water and tetralin gave somewhat lower conversion with the Wyodak coal, but the pressure was lowered by a large factor. Hydrogen was donated to the coal from the tetralin as well as from the water. Substituting an aromatic solvent or an alcohol solvent for the hydroaromatic tetralin gave lower conversions.

CO/water reductions of Blind Canyon bituminous coal in both water and water/tetralin mixture were also successful, but less so than the reactions of the Wyodak coal.

An understanding of how carbon monoxide reduces coal in this first-stage liquefaction process is essential for implementing improvements to the process and for designing effective catalysts. The reductive reactions catalyzed by the sodium aluminate in aqueous/carbon monoxide systems were investigated with various model compounds in order to learn more about the structure-reactivity parameters that may elucidate the nature of this reduction.

Reactions of polycyclic aromatic hydrocarbons in the CO/water/ NaAlO_2 system showed that those aromatics with linear arrangement (annellation) of the polycyclic rings are readily converted to hydroaromatics. The reactivities of the aromatics correlate with the ability to accept electrons (electron affinity) and form the radical anion intermediate. There also appears to be a reactivity factor involving addition of protons to the radical anion intermediate. Similar effects were noted for a series of aromatic ketones. The role of the sodium aluminate may involve forming a complex with the carbon monoxide that can more effectively donate electrons in the reaction. The effect of the sodium aluminate is not large, but it may be very important in optimizing the conversion of coal aromatic structures into hydroaromatic and other alkyl-bridged structures that are important in subsequent thermal or catalytic reactions.

Very great conversion effects for the sodium aluminate component were noted in the reactions of model carboxylic acids in the CO/water system. The nature of this catalytic effect is still under investigation. Evidence for a very large synergistic effect on diaryl ether hydrolysis was discovered for the combination of sodium aluminate with carboxylic acid groups.

2.0 GOALS AND OBJECTIVES

The efficient production of environmentally acceptable distillate fuels requires catalysts for hydrogenation and cleavage of the coal macromolecule and removal of oxygen, nitrogen, and sulfur heteroatoms. Currently, two-stage processes for coal conversion are under development. The first stage converts coal to a soluble form with minimal cracking and hydrogenation. This processing presently involves no catalyst other than the coal mineral matter present and the addition of a promoter, hydrogen sulfide, which may have a catalytic effect. The second stage involves hydrogenation upgrading of the first-stage product to distillates with fixed- or ebullated-bed catalysts.

The catalysts currently used in the second stage of coal liquefaction for hydrotreating the first-stage product are the same as those used in conventional petroleum refining; however, this application has not been very successful. Improvements in upgrading efficiency could be obtained if catalysts with longer life and better activity and selectivity were available. Rapid deactivation of the conventional Co-Mo and Ni-Mo catalysts on an alumina support have been attributed to coke formation (1), metals deposition (2), and inhibition of the active center by chemisorbed compounds (3). The objectives of this research project are to develop and test novel heterogeneous catalysts for hydrotreatment upgrading of first-stage coal liquefaction products. The new hydrogenation catalysts are based on pillared clays and hydrotalcites, which have very large micropore dimensions to accommodate the coal macromolecule, but yet do not possess strong acidic sites which lead to coking at high temperatures. A second objective is to develop a solid acid catalyst for depolymerization of the coal macromolecule. The acid catalysis process for coal liquefaction is believed to operate by ionic mechanisms. Some molten acids have successfully depolymerized coal, but the poor efficiencies of catalyst recovery and the corrosive nature of the catalyst make the process uneconomical. Stable solid acid catalysts will be developed which will avoid these difficulties. These catalysts are also based on pillared clays as well as on silica bases.

3.0 ACCOMPLISHMENTS

3.1 Introduction

The development of new catalysts for coal liquefaction was continued. The catalysts currently being investigated are basically homogeneous catalysts for first-stage coal solubilization and preliminary reduction.

Catalysis of the first stage of coal liquefaction involves improving the rates of bond cleavage reactions leading to improved solubility and of preliminary reduction reactions so that oils and asphaltene are produced without extensive retrogressive reactions. These materials should be able to

effectively interact with the solid and colloidal coal matter, catalyzing the conversion to soluble oils at moderate temperature, while minimizing problems with low surface areas or mass transfer. Thus various inorganic agents that are soluble in the reaction vehicle or solvent are being investigated. Some of these (e.g., sodium aluminate) are polymeric at the reaction conditions and are precursors for the clays and zeolites that are currently under investigation as second-stage liquefaction catalysts.

3.2 Experimental

The reagents bibenzyl, diphenyl sulfide, diphenyl ether, naphthalene, phenanthrene, anthracene, pyrene, fluoranthene, 1,2-benzanthracene, 2,3-benzanthracene, triphenylene, perylene, acetophenone, benzophenone, 1-acetonaphthone, 9-acetylanthracene, anthrone, benzanthrone, 1-methyl-naphthalene, 1-naphthoic acid, and 2-phenoxybenzoic acid were obtained from Aldrich.

3.2.1 Instrumentation

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with a Petrocol capillary column. A mixture of isooctane and n-octadecane was the internal standard. GC/FTIR/MS was performed on a Finnigan 800 ITD ion trap detector with a HP 5890A gas chromatograph and a J&W 30-m x 0.32-mm (ID), 1.0-micron film of DB-5. A 15-m x 0.25-mm (ID), 0.25-micron DB-5 film capillary column was used for the analysis of high boiling components.

3.2.2 Catalytic CO/Water Liquefaction of Coal

A slurry consisting of 5.0 g of coal (as received Wyodak-Clovis Point) and a solution of the catalyst in 20 g of water was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with a mixture of 1000 psi of desired gas. The reactor was heated to 400°C in a rocking autoclave (initial heatup time = 11 minutes) and left at this temperature for 30 minutes. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The reactor was attached to a set of two traps cooled in ice and liquid nitrogen. The product slurry was distilled to remove water and other volatile components. The distillate was saturated with NaCl and extracted with ether. The extract was mixed with the internal standards and analyzed by GC and GC/FTIR/MS. The residue from distillation of the water and volatiles was extracted with pentane, toluene, and tetrahydrofuran (THF). The pentane-soluble fraction was mixed with an internal standard and analyzed by GC. The toluene-soluble, THF-soluble, and THF-insoluble fractions were dried in vacuo at 110°C overnight and weighed. The weight of mineral matter and catalyst were subtracted from the dry weight of the THF-insoluble fraction to obtain the maf weight of unconverted coal, which was used in the calculation of percent conversion. The conversion to soluble material and the product fraction yield data are given in Table 1.

The workup procedure for the mixed water/organic solvent system was different in that the distillation was omitted, and pentane was added directly to the reaction product slurry. The slurry was thoroughly extracted with pentane and separated into the pentane-soluble fraction that included the organic solvent and the residue that included the water phase. The residue

TABLE 1
Catalytic Liquefaction of Coals

Reaction Temp. = 400°C, Reaction Time = 30 min Reductant gas (CO) = 1000 psi (at room temp.)						
Catalyst (mmol/g coal)	Coal (AR) (g)	Solvent(s) (g)	Conv.* (%)	Products (%)		
				Tol-S	THF-S	Pent-S**
NaAlO ₂ (0.5)	Wyodak (5.0)	Water (20.0)	89	20	27	42
NaAlO ₂ (0.5)	Wyodak (5.0)	Tetralin (5.2) Water (3.5)	79	19	30	30
NaAlO ₂ (0.5)	Wyodak (5.0)	1-MeNaph (5.0) Water (3.5)	71	11	27	33
NaAlO ₂ (0.5)	Wyodak (5.0)	Ethanol (5.1) Water (3.5)	75	14	28	33
NaVO ₃ (0.5)	Wyodak (5.0)	Tetralin (5.0) Water (3.5)	72	14	30	27
NaAlO ₂ (0.5)	Blind Canyon (5.3)	Water (20.0)	47	5	30	12
NaAlO ₂ (0.5)	Blind Canyon (5.4)	Tetralin (5.4) Water (3.6)	58	14	25	19

* = Conversions are based upon the amount of initial coal (maf).

** = Pentane solubles are by difference, also includes the products extracted by ether from the distillate.

was extracted with toluene, then THF as above. The water was extracted into the THF and was removed along with the THF by rotary evaporation.

In the workup of the experiment with the water/ethanol system, the initial extraction of the product slurry was carried out with toluene, and then pentane was added to the toluene extract to obtain the pentane-soluble fraction and the toluene-soluble (pentane-insoluble) fraction.

3.2.3 Catalytic CO/Water Reactions of Model Compounds

In a typical run, 0.5 g of model compound, 2 g of solvent(s), and the desired amount of catalyst were placed in a tubing bomb (12-mL microreactor). The microreactor was evacuated, pressurized with 1000 psig of carbon monoxide, placed in a rocking autoclave, and heated to 400°C. At the end of the

specified reaction period, the microreactor was cooled in a dry ice-acetone slurry, degassed, and opened. In the experiments with carboxylic acids, the resulting slurry was acidified with dilute HCl to convert any remaining carboxylate salts to the acid form. The desired amount of the internal standard was added to the product slurry, and the product slurry was extracted with dichloromethane or chloroform (for perylene and 2,3-benzanthracene products). The extract solution was dried over molecular sieves (4 Å) and analyzed by GC/FID and GC/FTIR/MS.

3.3 Results and Discussion

3.3.1 Catalytic CO/Water Liquefaction of U.S. Coals

In the first part of our study of homogeneous catalysts for first-stage coal liquefaction, catalysts for improving the conversion and product quality of liquefactions carried out in aqueous systems were investigated. Aqueous reactions that utilize carbon monoxide as the reductant gas have been extensively investigated in this and other laboratories over many years (4-6). Basic catalysts have been employed to achieve higher conversions. The aqueous/CO reduction has been shown to be superior to hydrogen for the first stage of liquefaction.

In screening a number of candidates for improving the conversion in aqueous/CO liquefaction processing, Jackson and others (7,8) found that aqueous sodium aluminate gave good conversions of brown coal to oils at temperatures of 350° to 400°C. Factors such as pH and concentration in aqueous systems of the materials are critical in determining the actual aluminate structures present (monomeric or polymeric); however, Jackson did not report the pH of his system. The sodium aluminate in some form could activate the carbon monoxide so as to produce an electron-, hydride-, or hydrogen-donating intermediate that would be a more effective reducing agent than the carbon monoxide without promoter.

Previous results have shown that the addition of sodium aluminate to the CO-water system improves the conversion of Wyodak subbituminous coal to distillate and soluble products at 400°C (9). In the current reporting period, the reactions of Wyodak and Blind Canyon coals with aqueous CO were conducted under various conditions to investigate the role of catalyst as well as solvent in determining the quality and yields of the liquefaction products. The reaction conditions and yield data are given in Table 1. Since high conversions to THF solubles are easily obtained at 400°C without any promoter or catalyst with the low-rank coals, the conversion to oils, asphaltenes, and distillate was accurately determined to evaluate the activity of sodium aluminate.

The conversion of Wyodak subbituminous coal to THF solubles in the aqueous/CO liquefaction with sodium aluminate was 89% (Table 1). This was substantially higher than that obtained with no added sodium aluminate (9). The high conversion with sodium aluminate is consistent with that observed by Jackson and others for Australian brown coals (7,8).

The composition of the distillate, oil, and asphaltene product obtained after first-stage liquefaction of Wyodak coal in aqueous CO was determined for comparison with that obtained previously in organic solvents with CO or with

hydrogen. These studies indicated that the volatile first-stage product from aqueous liquefaction contained large amounts of phenolics rather than hydrocarbons. This result offers the possibility in coal processing of removing the distillate and using it elsewhere, so that hydrogen needed for liquefaction is not wasted in deoxygenation of phenols.

Reactivity data for some other coals in CO/water/ NaAlO_2 were desired. Conversion of Blind Canyon (high volatile bituminous) coal with sodium aluminate catalyst was much lower than that of the Wyodak coal. Only 47% of the Blind canyon coal was converted to THF-soluble products under the same conditions. Tests with other coals will be carried out in the next year.

Sodium aluminate-catalyzed liquefaction of coals in the CO/water system is very effective, but high pressures are developed in the reactor. In order to lower the operating pressure, liquefaction of coal was conducted using a mixture of tetralin and water. Mixed solvent liquefaction of Wyodak coal was carried out by heating a well-mixed slurry of coal in aqueous sodium aluminate plus tetralin (5-g as-received coal/5-g tetralin/3-g water/2.5 mmol of sodium aluminate) for 30 minutes at 400°C in the presence of 1000 psig initial CO pressure. Compared with the CO/water system, CO/water/tetralin gave somewhat lower conversion (79%). The lower conversion could be related to the lower pressure. The pressure is below the critical pressure of the water, and different properties of the solvent, as well as of the solute species, would be expected.

In contrast, the use of a mixed solvent in the liquefaction of Blind Canyon bituminous coal with sodium aluminate catalyst significantly improved the conversion (58%) compared with the liquefaction in water solvent (Table 1). However, the conversion is still lower than that obtained with Wyodak subbituminous coal. This result indicates that there may be complex phase problems with regard to the solvents, and each coal will require experimentation to determine optimum solubilization parameters.

Current liquefaction processes generally utilize a hydrogenated recycle solvent containing hydroaromatics that could serve as hydrogen donors. The tetralin used in the experiments above was intended to model this behavior. However, a nonhydrogenated solvent could be used in processing if it gave equivalent conversions and product quality in the CO/mixed water-organic solvent liquefaction. In order to determine the effects of the type of organic solvent on yields and product quality in mixed water-organic solvent liquefaction, the reactions of Wyodak coal were carried out in mixed solvents composed of water plus 1-methylnaphthalene and water plus ethanol, under reaction conditions similar to the water/tetralin reaction described above. Sodium aluminate-catalyzed liquefaction of Wyodak coal in water/1-methylnaphthalene and water/ethanol solvent systems gave 71% and 75% conversions, respectively. Compared with the water/tetralin system, water/1-methylnaphthalene and water/ethanol gave lower conversions. It should also be pointed out that in the water/tetralin system, some of the tetralin was converted to naphthalene (see discussion below); thus the tetralin played some role in hydrogenating, donating hydrogens to the first-stage liquefaction product. The reduced yields obtained with the aromatic and alcohol solvents mean that better results will probably be obtained in a process that uses a hydrogenated recycle solvent, as in the current Wilsonville art.

The liquefaction product quality as determined by the distribution of solubility fractions was good for the sodium aluminate-catalyzed reaction. As shown in Table 1, the toluene solubles amounted to 20% of the maf coal, and 42% of the coal was converted pentane solubles, CO₂, and H₂O. The major products in the distillate were oxygenated compounds, such as methanol, 2-propanol (from acetone), and phenolics. In addition, there were hundreds of hydrocarbon components that are typically found in coal-derived products. However, the reaction in the water/tetralin system gave a significantly lower yield of pentane-soluble products. Yields of toluene and THF-soluble materials were comparable. The amount of phenol was slightly lower, but the amounts of alkylphenols were significantly higher. Total phenolics amounted to ca. 6% of the starting maf weight of coal.

The composition of the solvent and solvent-derived species was determined for the water/tetralin liquefaction experiments to define the role of the hydroaromatic solvent, if any, in the first-stage process. The ratio of tetralin/naphthalene was 20, indicating that approximately 5% of the tetralin was converted into naphthalene. This means that hydrogen transfer from tetralin occurs during liquefaction. A large number of alkyltetralins and alkyl naphthalene were also found, probably some by addition to the solvent and some from depolymerization of the coal.

Reactions in water/1-methylnaphthalene gave significantly lower conversion to toluene-soluble products. Thus the effect of the reaction solvent on the product appears to be related more to the higher molecular weight species, increasing their solubility by hydrogen donation or adduction. Compared with water/tetralin solvents, the amount of phenol was lower, but the amount of alkylphenols was significantly higher for the water/1-methyl-naphthalene solvent. A large number of alkyl naphthalenes were formed.

The reaction of Wyodak coal in water/ethanol gave a product distribution similar to that obtained from the water/1-methylnaphthalene system. However, the amount of phenol and cresols was significantly lower than that obtained from water only or water/tetralin and water/1-methylnaphthalene reactions. This is perhaps due to the mineral-catalyzed conversion of phenolics to ethylphenols in the supercritical ethanol.

Compared with Wyodak coal, sodium aluminate-catalyzed liquefaction of Blind Canyon coal gave a very low conversion to toluene- and pentane-soluble products. The water/tetralin solvent system significantly improved the conversion to toluene and pentane-soluble materials, whereas the yield of THF-soluble material decreased. Analysis of the pentane-soluble materials from calibrated GC data indicated that only 2% of the coal was converted to phenolic materials. Based on the retention time of the components, it is concluded that Blind Canyon (bituminous coal) produced higher molecular weight products than the Wyodak subbituminous coal during CO/water liquefaction.

3.3.2 CO/Water Reactions of Model Compounds

An understanding of how carbon monoxide reduces coal in first-stage liquefaction is essential for implementing improvements to the process and designing effective catalysts. Why does CO give better conversions to soluble materials than hydrogen? After several decades, little is understood about the mechanism of the aqueous CO reaction with coal or even with model organic

compounds. Jones and others have shown that an aryl ketone (benzophenone) and an aryl carbinol are reduced (10). Bases were required for reduction of the ketone, and higher conversions were obtained for the carbinol reduction in the presence of base. Reduction of anthracene and quinoline were also effected with aqueous CO; however, higher conversions of anthracene were obtained in the absence of base (11). The reduction of ketones with CO in aqueous sodium carbonate was explained by sodium ion activation of the CO to give an intermediate such as formate that can donate hydride to the carbonyl. Reduction of anthracene or other hydrocarbons would appear to proceed by a different mechanism.

The second priority in our program was to understand something about the activation of CO and the nature of the sodium aluminate catalysis. Sodium aluminate could probably activate CO for hydride reduction of ketones as well as sodium carbonate, perhaps better. But does it also activate CO so that hydrogenation of hydrocarbons occurs? Can it lower activation energies for cleavage of bonds such as in ether and carboxylate groups? The reactions of several model compounds were investigated in aqueous/CO conditions, and the results were compared with those obtained in the absence of the sodium aluminate.

3.3.2.1 Catalytic Hydrogenation of Polynuclear Aromatic Hydrocarbons

Naphthalene, anthracene, phenanthrene, pyrene, fluoranthene, triphenylene, perylene, 1,2- and 2,3-benzanthracene were used as test compounds to investigate the hydrogenation of a polynuclear aromatic system by an aqueous CO system (Table 2).

Naphthalene was not reduced by the CO/water system at 400°C with or without the addition of sodium aluminate catalyst. In contrast, anthracene was quite reactive under these conditions, as described in the previous report (9). This earlier work demonstrated that higher conversions of anthracene were obtained with sodium aluminate than without this catalyst. But lower conversions were obtained with sodium hydroxide, which was consistent with the results Stenberg reported for reactions with a similar base, sodium carbonate, at higher temperatures.

The conversion data for other polynuclear aromatic compounds, which were obtained in this quarter (Table 2), further demonstrated a wide divergence in reactivity. Phenanthrene, pyrene, fluoranthene, and perylene were not very reactive. Thus additions of rings (annellations) to the naphthalene structure that are nonlinear do not significantly increase the reactivity, but linear benzannellation, as in the anthracene structure, results in a significant increase in reactivity.

This structural effect on reactivity of the polynuclear aromatics is further demonstrated in the benzanthracene series. 2,3-Benzanthracene, which contains the linear polynuclear aromatic system, gave a very high (94%) conversion to the dihydrogenated product. The nonlinear benzannellated isomer, 1,2-benzanthracene, was less reactive (10% conversion) than anthracene. Thus the effect of linear versus nonlinear benzannellation on the

TABLE 2
CO/Water Hydrogenation of Polynuclear Aromatic Hydrocarbons

Reaction Temp = 400°C, Reaction Time = 2 hr Reductant (CO) = 1000 psi			
Catalyst (mmol/g substr)	Substrate (mmol)	Conv. (%)	Major Products (mmol)
NaAlO ₂ (0.50)	Naphthalene (3.90)	<1	Tetralin (trace)
NaAlO ₂ (0.50)	Anthracene (2.77)	82	9,10-Dihydroanthracene (2.19) Tetrahydroanthracene (0.13)
NaAlO ₂ (0.5)	Phenanthrene (2.81)	2	Dihydrophenanthrene (trace)
NaAlO ₂ (0.5)	Pyrene (2.52)	4	Dihdropyrene (0.04) Tetrahydropyrene (0.01)
NaAlO ₂ (0.50)	1,2-Benzanthracene (0.44)	10	Dihydro 1,2-Benzanthracene (0.04)
NaAlO ₂ (0.50)	2,3-Benzanthracene (0.44)	94	Dihydro 2,3-Benzanthracene (0.36)
NaAlO ₂ (0.50)	Fluoranthene (2.47)	<1	None
NaAlO ₂ (0.50)	Perylene (0.40)	3	Hydroperylene (trace)

reactivity behavior in the anthracene series is consistent with that reported above for other aromatics.

These reactivity data suggest that certain (linear) aromatic structures in coals might be expected to be reduced in a first-stage liquefaction process that uses CO as the reducing gas. Although "deep" reduction of aromatics does not proceed, hydrogen is added at critical sites in the structures, and the resulting hydroaromatic structures may be effective in promoting further reactions such as radical capping and in preventing retrograde reactions that may occur during thermal processing. The effects of substituents on the reactivity of the aromatics were not studied, but since reactivities are usually affected significantly by substituents, especially heteroatoms, the reduction of these types of structures in coal in the catalytic CO/water system is even more likely.

Correlations of the reactivity data with other chemical properties of the polynuclear aromatics may also provide important clues as to the nature or mechanism of the CO/water reduction. The high reactivity of anthracene and other linear polynuclear aromatics in the reduction reaction suggests that a relationship of the observed reactivity of the aromatic hydrocarbon with the electron affinity (EA) of the hydrocarbon may be significant. The reaction of the aromatic compounds with the reducing agent (CO or complexed CO) may

transfer a single electron to initially form a radical anion intermediate. The most reactive aromatics would be those with the highest electron affinities. Since various methods have been used for determining electron affinities, various compilations of electron affinities exist with different values. In Table 3 the electron affinities of various polynuclear aromatics are reported along with the corresponding conversions in the CO/water/ NaAlO_2 system. Values for cathodic reduction potentials ($E_{1/2}$) are also available and are listed in Table 3.

Aromatic compounds with positive electron affinities have a low-energy lowest unoccupied molecular orbital (LUMO) for accepting an electron. Because of the relatively high LUMO energies for benzene and naphthalene, the electron affinities for unsubstituted benzene and naphthalene are low or negative, depending on the type of measurement; hence, under some conditions, the corresponding radical anions are unstable. More highly conjugated or substituted aromatics will have a lower-energy LUMO and, consequently, have positive electron affinities.

Although a regression analysis has not been performed, there appears to be a correlation of the conversion data with the EA values determined from the lowest-energy UV band (12,13). The low reactivities for naphthalene, phenanthrene, triphenylene, and pyrene are correctly predicted from the low EA values. The high reactivities for anthracene, 2,3-benzanthracene, and 1,2-benzanthracene are also predicted in the correct order. Only the perylene EA value does not seem to be consistent with the low reactivity observed in the CO/water system. The EA values from the 0-0 transition (13) for naphthalene, anthracene, phenanthrene, and triphenylene also appear to correlate with the reactivities, but the EA values of pyrene, perylene, and 1,2-benzanthracene are too large for the observed reactivities of these compounds in this system. Other EA values calculated from molecular orbital theory are also consistent with the observed reactivities (14). The half-wave reduction potentials ($E_{1/2}$) of the aromatic compounds (15) do not appear to

TABLE 3

CO/Water Conversions and Electron Affinities of Polynuclear Aromatics

Substrate	Conv.	EA (12,13)	EA (13)	EA (14)	$E_{1/2}$ (15)
Naphthalene	<1	-0.40	-0.12	-0.38	1.98
Anthracene	82	0.50	0.42	0.49	1.46
Phenanthrene	2	-0.31	0.20	-0.20	1.94
Triphenylene		-0.41	0.14	-0.28	1.97
Pyrene	4	0.09	0.39	0.68	1.61
Fluoranthene	<1				1.35
Perylene	3	0.75		0.80	1.25
1,2-Benzanthracene	10	0.29	0.46	0.62	1.53
2,3-Benzanthracene	94	0.92	0.98	0.82	1.14

give as good a correlation with the reactivities. This may be due to additional surface and solvent effects that occur during the electrode potential measurements.

A process involving single electron transfer (SET) from CO or a CO aluminate complex to the aromatic substrate is consistent with the reactivity data. With some aromatic compounds, the resulting radical anion may react rapidly with water or hydroxyl such that a hydrogen ion (H^+) is transferred. The rate of this protonation reaction may differ considerably for the various anion radical intermediates. In fact, the rate constants for protonation of perylene and fluorene radical anions are much lower than those of other aromatics (16). This may explain their lack of reactivity in the CO/water reduction tests discussed above. As in some other SET reactions, the hydrogen ion could begin bonding synchronously with the electron transfer in the more reactive aromatics (17). The radical resulting from the H^+ transfer will then react further with an electron donor to give the carbanion intermediate which is again protonated. Further study of structure-reactivity data is needed to refine the SET concept for CO/water reductions.

The nature of the complexation products of CO with metal oxides has been investigated under anhydrous conditions (18,19). These surface bound species exhibit spectra consistent with dimeric or polymeric structures which may be paramagnetic. The structures of CO/metal oxide complexes present in high-temperature hydrous conditions are unknown, but the possibility exists that the unpaired electrons on the CO ligand are involved in SET reduction of the aromatic compounds.

3.3.2.2 Catalytic Reduction of Ketones

The reactions of ketones with CO/water were also investigated as models for possible reactions that would occur in coal liquefaction (Tables 4 and 5). Since most of the aryl ketones have a high electron affinity, the reaction temperature was reduced to 350°C, so that structure-reactivity effects could be more easily distinguished.

The reduction of anthrone in CO/water with sodium aluminate catalyst was slightly greater than in the reaction without sodium aluminate. The major products were anthracene and dihydroanthracene. The intermediate alcohol reduction product (anthrol) was not obtained, because it very rapidly dehydrates to anthracene. Dihydroanthracene could have formed by reduction of anthracene, which occurs readily (see discussion above), or possibly by reduction of a carbonium ion intermediate that forms when the alcohol intermediate eliminates hydroxyl.

The reduction of anthrone was also carried out in the mixed water/tetralin solvent system. The conversion decreased by 10%, which is consistent with the decrease observed in the coal conversion in the same solvent system. The decrease can be attributed to either the lower pressure of the system, which results in lower concentration of electron donor (CO complex), or to a phase separation problem that is not currently understood.

The amount of benzophenone converted to reduced products with sodium aluminate catalyst was similar to that found for anthrone (53%). The reduction products are quite different in nature, however. The alcohol

TABLE 4

CO/Water Reductions of Anthrone

Reaction Temp. = 350°C, Reaction Time = 2 hr Reductant (CO) = 1000 psi				
Catalyst (mmol/g substr)	Substrate (mmol)	Solvent (g)	Conv. (%)	Major Products (mmol)
None	2.58	Water (2.01)	49	Anthracene (0.57) Dihydroanthracene (0.35)
NaAlO ₂ (0.50)	2.58	Water (2.04)	52	Anthracene (0.62) Dihydroanthracene (0.39)
NaAlO ₂ (0.50)	2.58	Water (0.3) Tetralin (0.5)	42	Anthracene (0.33) Dihydroanthracene (0.30) Tetrahydroanthracene (0.02)

TABLE 5

CO/Water Reduction of Ketones

Reaction Temp. = 400°C, Reaction Time = 2 hr Solvent (water) = 2 g, Reductant (CO) = 1000 psi				
Catalyst (mmol/g substr)	Substrate (mmol)	Conv. (%)	Major Products (mmol)	
None	Benzophenone (2.64)	37	Diphenylmethane (0.70) Benzhydrol (0.22)	
NaAlO ₂ (0.50)	Benzophenone (2.70)	53	Diphenylmethane (0.94) Benzhydrol (0.46)	
NaAlO ₂ (0.5)	Acetophenone (4.17)	55	Ethylbenzene (0.36) Styrene (0.66) 1-Phenylethanol (0.73) Phenol (0.06) Benzene (trace) Toluene (trace)	
NaAlO ₂ (0.50)	1-Acetonaphthone (3.00)	53	1-Ethyl-naphthalene (0.68) 1-Vinylnaphthalene (0.52) 1-Methylnaphthalene (0.05) Naphthalene (0.03) 1(1-naphthyl) ethanol (0.13)	
NaAlO ₂ (0.50)	9-Acetylanthracene (0.45)	77	Anthracene (0.17) Dihydroanthracene (0.13) Ethylanthracene (0.03)	
NaAlO ₂ (0.50)	9-Fluorenone (0.60)	89	Fluorene (0.26) 9-Fluorenol (0.18)	
NaAlO ₂ (0.50)	Benzanthrone (2.16)	100	Dihydrobenzanthracene (2.00)	

product (benzhydrol) was present, since it does not eliminate hydroxyl to form a stable aromatic compound as in the anthrone system. Instead, elimination of hydroxyl resulted in reduction to diphenylmethane. The reduction of benzophenone in the absence of sodium aluminate was lower than that observed for anthrone.

The conversion of fluorenone to reduced products was substantially higher than observed for anthrone. About the same ratio of alcohol to methylene product was found. The more favorable electron affinity is due to the higher stability of the fluorenyl anion system. A low-energy LUMO is also present in the polycyclic benzanthrone, which was completely reduced by the CO/water/ NaAlO_2 system.

A comparison of the reactivity of the series of aryl methyl ketones was also conducted with interesting results. Reduction of a single aryl ring ketone (acetophenone) was effected in 55% conversion to give a mixture of products. The intermediate alcohol was present, and this product was further converted to styrene via elimination of the hydroxyl group. Besides the styrene, a substantial amount of ethylbenzene was formed. Reduction to the methylene could have occurred via the intermediate carbonium ion or perhaps by reduction of styrene.

Acetonaphthone exhibited a similar reactivity, giving 52% conversion to a similar mixture of products. As expected, the ketone group was reduced, and the naphthalene rings were not reduced, owing to the low electron affinity of the naphthalene system. In addition to the alcohol, vinylnaphthalene, and ethylnaphthalene, a very small amount of methylnaphthalene and naphthalene were formed. 9-Acetylanthracene gave a high conversion (77%) to products. In this case, the more easily reduced anthracene moiety generated some additional reaction pathways, including hydrocracking of the aryl-alkyl bond. Ethylanthracene from reduction of the aceto group was a minor product. Anthracene was major product, which may have formed via elimination of the ethyl group from the intermediate radical, 10-hydro-10-ethyl-9-anthracenyl. Anthracene was then further reduced to dihydroanthracene.

The results of the model ketone reductions suggest that the CO/water/ NaAlO_2 reduction of coals that are believed to contain significant amounts of aryl ketones will also produce significant reduction to less oxygenated and perhaps hydroaromatic structures. The presence of these structures may significantly lower the tendency of coal materials to undergo retrograde condensation reactions during further thermal and catalytic cracking reactions. Further work with quinones is planned so that we can determine whether the products from these reactions with CO/water will also be less likely to participate in the retrograde reactions.

3.3.2.3 Catalytic Hydrocracking of Model Compounds

The hydrocracking activity of the sodium aluminate-catalyzed CO/water system was investigated using bibenzyl, diphenyl sulfide, and diphenyl ether as the test compounds. The reaction of bibenzyl was carried out at 425°C for 2 hours with aqueous sodium aluminate in the presence of 1000 psig initial CO pressure. A higher temperature was used, since the amount of hydrocracking observed in the studies discussed above was very small at those temperatures. The conversion data are given in Table 6. The conversion of bibenzyl was 37%,

TABLE 6
CO/Water Hydrocracking of Model Compounds

Reaction Temp. = 425°C, Reaction Time = 2 hr Solvent (water) = 2 g, Reductant (CO) = 1000 psi				
Catalyst (mmol/g substr)	Substrate (mmol)	Temp. (°C)	Conv. (%)	Major Products (mmol)
NaAlO ₂ (0.5)	BB (2.78)	425	37	Benzene (0.21) Toluene (0.35) Ethylbenzene (0.15)
None	DPE (2.90)	350	2	Benzene (trace)
NaAlO ₂ (0.50)	DPE (2.29)	350	3	Benzene (trace)
None	DPS (2.78)	425	18	Benzene (0.54)
NaAlO ₂ (0.50)	DPS (2.74)	425	28	Benzene (0.70)

BB = Bibenzyl.
DPE = Diphenyl ether.
DPS = Diphenyl sulfide.

which is comparable with sodium carbonate-catalyzed reactions (20). The major products were benzene, toluene, and ethylbenzene. Stenberg and coworkers have investigated the reduction of bibenzyl using sodium carbonate, alkaline earth oxides, and fly ash as disposable catalysts in carbon monoxide-water systems (20).

Stenberg and coworkers reported that CO-water effectively cleaves aryl-sulfur bonds in diphenyl sulfide (64.4% conversion) at 425°C in CO-water for a 2-hr reaction. Addition of sodium carbonate results in lower conversion (47%) of diphenyl sulfide (21). However, we found conversions of only 18% for diphenyl sulfide in reactions without sodium aluminate under the above conditions. Addition of sodium aluminate significantly improved the cleavage of the aryl-sulfur bond as indicated by 28% conversion. Benzene was the only reaction product.

The reaction of diphenyl ether in CO-water with and without sodium aluminate was carried out at 350°C for 2 hours in the presence of 1000 psi of initial CO pressure. The results indicated that CO-water both with and without sodium aluminate promoter did not cleave the aryl-oxygen bond.

3.3.2.4 Catalytic Decarboxylation of Carboxylic Acids

The decarboxylation of carboxylic acids was investigated by using carboxylic acid substrates, 2-benzylbenzoic acid (2-BBA), 2-phenoxybenzoic

acid (2-PBA), and 1-naphthoic acid as the test compounds to determine if there are any catalytic effects on decarboxylation or other reactions that might occur on heating carboxylic acids. Reactions of these compounds were carried out at 350°C for 2 hours in the presence of 1000 psi of CO initial pressure. Reactions of 1-naphthoic acid were also conducted at 300°C. Due to analytical difficulties in accurately determining the amount of carboxylic acids, the product yield was used to determine percent conversion of the carboxylic acids. Reaction conditions and conversion data are given in Table 7.

The reaction of naphthoic acid in CO-water gave 10% and 18% conversions of 1-naphthoic acid into products at 300° and 350°C respectively. The major product was naphthalene. The addition of sodium aluminate increased the conversion to 17% and 37% for 300° and 350°C reactions, respectively. The dramatic catalytic effect of the sodium aluminate on decarboxylation may have a very important role in first-stage liquefaction, and more efforts to understand this effect are in progress. In addition to naphthalene (major product), trace amounts of tetralin were also formed in the sodium aluminate-catalyzed reactions. It is not known whether the naphthalene reduction

TABLE 7
CO/Water Reactions of Naphthoic Acid

Reaction Time = 2 hr, Reductant (CO) = 1000 psi					
Catalyst (mmol/g substr)	Substr. (mmol)	Temp. (°C)	Solvent (g)	Conv. (%)	Major Products (mmol)
None	2.95	300	Water (2.10)	10	Naphthalene (0.17)
NaAlO ₂ (0.50)	2.92	300	Water (2.02)	17	Naphthalene (0.23) Tetralin (trace)
NaOH (0.50)	2.80	300	Water (2.00)	9	Naphthalene (0.12)
NaAlO ₂ (0.50)	2.81*	300	Water 2.00	12	Naphthalene (0.16)
None	0.70	350	Water (2.02)	18	Naphthalene (0.12) Tetralin (0.01)
NaAlO ₂ (0.50)	0.70	350	Water (2.00)	37	Naphthalene (0.18) Tetralin (0.01)
NaAlO ₂ (0.5)	0.70	350	Water (0.30) Tetralin (0.50)	19	Naphthalene (0.31) Tetralin (3.6)
NaAlO ₂ (0.50)	0.73*	350	Water (2.00)	19	Naphthalene (0.14) Tetralin (0.04)

* = Sodium naphthoate was used as the substrate.

occurred before or after decarboxylation. The sodium aluminate-catalyzed reaction of naphthoic acid in the water/tetralin system gave lower conversion (19%) than the reaction in water. It is clear that higher temperatures are required for better decarboxylation kinetics for this type of acid. Thus future work will be conducted at 385° and 400°C.

The CO/water reaction with sodium hydroxide in place of sodium aluminate gave lower conversions (9%) of acid at 300°C into naphthalene. Also, sodium hydroxide was added to the naphthoic acid to form sodium-1-naphthoate, and this salt was tested with sodium aluminate to give 12% and 19% conversions at 300° and 350°C, respectively. These reactions exhibit the lower reactivity of the carboxylate salt compared with the carboxylic acid form.

Besides catalyzing the decarboxylation of carboxylic acids, sodium aluminate may also have an effect on reactions of polyfunctional groups in the coal. The possibility also exists that the aluminate could moderate the alleged cross-linking effects during thermal treatments of coal. Therefore, carboxylic acids that have the potential for cross-linking or undergoing other reactions were investigated (Table 8).

In contrast to the reaction of naphthoic acid, the reaction of 2-phenoxybenzoic acid with CO-water at 350°C for 2 hr (no sodium aluminate) resulted in almost complete decarboxylation. The phenoxy group thus increases the decarboxylation reactivity of the acid group by an electronic substituent effect. The reaction was accompanied by a small amount of reduction of the diaryl ether linkage to give benzene and phenol. No products resulting from the addition of species derived from the carboxylate group to the adjacent ring to give a cyclic structure such as dibenzofuran or xanthone were observed. Thus no evidence for a cross-linking type of activity during decarboxylation could be obtained.

TABLE 8
CO/Water Reactions of Substituted Carboxylic Acids

Reaction Temp. = 350°C, Reaction Time = 2 hr Solvent (water) = 2 g, Reductant (CO) 1000 psi			
Catalyst (mmol/g Substrate)	Substrate (mmol)	Conversion (%)	Major Products (mmol)
None	2-PBA (2.37)	96	Benzene (0.05) Phenol (0.13) Diphenyl ether (1.82)
NaAlO ₂ (0.50)	2-PBA (2.27)	100	Phenol (2.37) Diphenyl ether (0.85)
None	2-BBA (2.40)	5	Diphenylmethane (0.11)
NaAlO ₂ (0.50)	2-BBA (2.29)	10	Diphenylmethane (0.22)

In the CO/water reaction of 2-phenoxybenzoic acid with added sodium aluminate, a large portion of the substrate underwent a hydrolysis reaction of the diaryl ether to give phenol as the major product. Since the hydrolysis reaction did not occur in the sodium aluminate-catalyzed reaction of diphenyl ether (see discussion above), the significant change in the reactivity of the ether oxygen could be attributed to the effect of the ortho-carboxylate group in the presence of sodium aluminate. Perhaps this effect results from the formation of a complex of the aluminate with the carboxylate that can catalyze the hydrolysis reaction. Again, no cyclic structures were found in the products.

The reaction of 2-benzylbenzoic acid with CO-water gave only 5% conversion of acid to diphenylmethane. Addition of sodium aluminate increased the conversion to 10%. Decarboxylation was slow for this substrate, but, as in the case of naphthoic acid, the addition of sodium aluminate improved the reactivity by a large factor. No cracking of the arylmethylen bond of the 2-benzylbenzoic acid occurred in these reactions, and only a trace of anthracene resulting from cyclization was found.

4.0 REFERENCES

1. Derbyshire, F. *ACS Div. of Fuel. Chem. Preprints* **1988**, 33 (3), 188.
2. Garg, D.; Givens, E.N. *Fuel Proc. Technol.* **1984**, 9, 29; Kovach, S.M.; Castle, L.J.; Bennett, J.V.; Svrodt, J.T. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, 17, 62.
3. Mills, G.A.; Beodeker, E.R.; Oblad, A.G. *J. Amer. Chem. Soc.* **1950**, 72, 1554.
4. Appell, H.R.; Wender, I.; Miller, R.D. *Prep. Pap.--Am. Chem. Soc., Div. of Fuel Chem.* **1969**, 13, 39-44.
5. Sondreal, E.A.; Knudson, C.L.; Schiller, J.E.; May, T.H. *In Proceedings of the 9th Biennial Lignite Symp.: DOE/GFERC/IC-77/1*, 1977, pp 129-158.
6. Ross, D.S.; Green, R.K.; Monsani, R.; Hum, G.P. *Energy Fuels* **1987**, 1, 287.
7. Jackson, W.R.; Lim, S.C.; Stray, G.J.; Larkins, F.P. *In Proceedings of the 1989 International Conference on Coal Science; Tokyo, Dec. 1989, Vol. II*, pp 815-818.
8. Hughes, C.P.; Sridhar, T.; Chuan, L.S.; Redlich, P.J.; Jackson, W.R.; Larkins, F.P. *USA/Australia Workshop on Use of Low-Rank Coals; Billings, MT, May 1991*.
9. Olson, E.S.; Sharma, R.K. "Semiannual Technical Progress Report for the Period July-December 1991," Energy and Environmental Research Center, 1991.
10. Jones, D.; Baltisberger, R.J.; Klabunde, K.J.; Woolsey, N.F.; Stenberg, V.I. *J. Org. Chem.* **1978**, 43, 175-177.

11. Stenberg, V.I.; Wang, J.; Baltisberger, R.J.; Van Buren, R.; Woolsey, N.F. *J. Org. Chem.* **1978**, *43*, 2991-2994.
12. Matsen, F.A. *J. Chem. Phys.* **1956**, *24*, 602.
13. Becker, R.S.; Wentworth, W.E., *J. Am. Chem. Soc.* **1962**, *85*, 2210-2214.
14. Hedges, R.M.; Matsen, F.A. *J. Chem. Phys.* **1958**, *28*, 950.
15. Chilton, H.T.J.; Gowenlock, B.G. *Trans. Faraday Soc.* **1954**, *50*.
16. Levanon, H.; Neta, P.; Trozzolo, A.M. In *Organic Free Radicals*. ACS Symp. Series 69; Pryor, W.A., ed.; Amer. Chem. Soc. Washington D.C., 1978, pp. 401-409.
17. Pross, A. *Acc. Chem Res.* **1985**, *18*, 212-219.
18. Morris, R.M.; Kaba, R.A.; Groshens, T.G.; Klabunde, K.J.; Baltisberger, R.J.; Woolsey, N.F.; Stenberg, V.I. *J. Amer. Chem. Soc.* **1980**, *102*, 3419-3424.
19. Guglielminotti, E.; Coluccia, S.; Garrone, E.; Cerruti, L.; Zecchina, A. *J. Chem. Soc. Faraday Trans.* **1979**, *1*, 96.
20. Stenberg, V.I.; Baltisberger, R.J.; Knittel, D.; Wettlaufer, D.; Woolsey, N.F.; Knudsen, C. 14th Intersociety Confr., Aug 5-10, 1979, Boston, MA.
21. Stenberg, V.I.; Baltisberger, R.J.; Klabunde, K.J.; Woolsey, N.F.; Severson, D.; Souby, M. "Quarterly Technical Progress report for the Period July-September 1978," Contract No. EX-76-C-01-2211.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORTFORM APPROVED
OMB NO. 1800-0127
Page 1 of 2

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Liquefaction Reactivity of Low-Rank Coals (3.4)	3. Reporting Period 3-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-86
		6. Completion Date 9-30-92

7. FY 91/92	8. Months or Quarters Quarters	1991 JUL AUG SEP OCT NOV DEC												1992 JAN FEB MAR APR MAY JUN							
9. Cost Status	a. Dollars Expressed in Thousands	b. Dollar Scale																			
10. Cost Chart
Fund Source			Quarter				Cum. to Date	Tot. Plan													
			1st	2nd	3rd	4th															
DOE			P	37	37	37	36	147	147												
			A	27	22	24	23	96													
			P																		
			A																		
			P																		
			A																		
			P																		
			A																		
Total P				37	37	37	36	147	147												
Total A				27	22	24	23	96													
Variance				10	15	13	13	51													
P = Planned A = Actual																					
Total Planned Costs for Program/Project \$147			c. Cumulative Accrued Costs																		
			Planned				37			74			111			147					
			Actual				27			49			73			96					
			Variance				10			25			38			51					

11. Major Milestone Status	Units Planned	
	Units Complete	
Task 1:		
A. Testing Aluminates with Low-Rank Coal	P	1 ▽ 2 ▽ 3 ▽ 4 ▽ 5 ▽
	C	
	P	
	C	
B. Testing of Heteropolymers	P	1 ▽ 2 ▽ 3 ▽
	C	
	P	
	C	
C. Testing with Colloidal Coal	P	1 ▽
	C	
	P	
	C	
D. Mechanism Studies	P	1 ▽ 2 ▽
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks Due to EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.	
13. Signature of Recipient and Date <i>Chun S. Olson</i> 7-30-92	14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

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				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task 1					
A.	Testing Aluminates with Low-Rank Coal:				
1.	Effects of pH	9-30-91	12-31-91		
2.	Effects of concentration	10-31-92			
3.	Effects of temperature	11-30-91	3-31-92		
4.	Effects of catalyst aging	1-31-92			
5.	Reuse of water/aluminate	2-29-92			
B.	Testing of Heteropolymers:				
1.	Aluminum with phosphorus	3-31-92			
2.	Aluminum with silicon or aluminum with titanium	4-30-92			
3.	Aluminum with other metals	6-30-92			
C.	Testing with Colloidal Coal	12-31-91			
D.	Mechanism Studies:				
1.	Extent of decarboxylation	1-31-92	3-31-92		
2.	Model compound tests	5-31-92	6-30-92		
Task 2	Final Project Report	8-31-92			

3.5 Gasification Ash and Slag Characterization

GASIFICATION ASH AND SLAG CHARACTERIZATION

Semiannual Technical Progress Report
for the Period January 1, 1992, through June 30, 1992

by

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for

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GASIFICATION ASH AND SLAG CHARACTERIZATION

1.0 TASK I: THERMAL CONDUCTIVITY OF COAL ASHES

1.1 Introduction

In combustion and gasification systems, a buildup of deposits on heat-transfer surfaces in the convective pass reduces the heat transfer. Therefore, it is important to know the thermal conductivity of the deposited coal ashes to predict the energy loss on the boiler tube heat-transfer surfaces. In this project the Energy and Environmental Research Center (EERC) has developed an apparatus to measure the thermoconductivity of coal ashes.

The thermal conductivity is defined as the proportionality coefficient between the heat flux passing through a material and the temperature gradient resulting from the causative heat flux. This arises from the lattice thermal conduction, k_l ; the electronic thermal conduction, k_e ; and ionic thermal conduction, k_i (1). The latter factor usually occurs at high temperatures and is a result of the transport of mobile alkali metal ions.

$$k = k_l + k_e + k_i \quad [\text{Eq. 1}]$$

The primary concern when trying to measure thermoconductivity is to obtain a controlled heat flow in a prescribed direction such that the actual boundary conditions in the experiment agree with those assumed in the theory. The appropriate method is determined by the physical nature of the material, the geometry of the samples available, the required accuracy of results, the speed of operation, and the time and funds available. The various methods for the measurement of thermal conductivity fall into two categories: the steady-state and the nonsteady-state methods. The steady-state method is appropriate for materials of low thermal conductivity such as coal ashes. The measurements of thermal conductivity under steady-state conditions require guard heaters (combined with thermal insulation in most cases). The supplied heat must flow through the defined area of the sample without gain or loss. To achieve such precise conductivity in practice is simply impossible. However, from the practical point of view, it is important to carry out experiments under the same conditions to allow reliable comparison of obtained results. The nonsteady-state method is applied to measure thermal diffusivity (2,3).

The heat flux, defined as Q/t , can result from radiative heat. This effect is mostly observed in large sample sizes (4). Also, one measurement on a large sample takes a long time. Based on the literature, generally a small length-to-width ratio for samples which are poor conductors is recommended to measure thermal conductivity at high temperatures (2,3). To minimize errors in temperature gradient measurements and save time, the thin-plate method was selected for thermal conductivity measurements. The applied method is based on the assumption that there is the same heat flow, Q , through both a sample of unknown conductivity and a standard of known conductivity (5).

Very little data on thermal conductivity of coal ashes exist in the open literature. The problems with obtaining good data on ashes are related to the

extremely inhomogeneous chemical and mineralogical compositions present in coal ashes. The purpose of this work is twofold: 1) to gain an understanding of the effects of inhomogeneity, crystallinity, and porosity of coal ash deposits on heat-transfer phenomena; and 2) to determine the relationship between thermal and electrical conductivities in sintered coal ashes in the temperature range of 25°-500°C. To accomplish these objectives, special care was taken with sample preparation.

1.2 Experimental Apparatus

Thermal conductivity measurement was based on the axial one-dimensional heat flow method (6,7). The apparatus used for the thermal and electrical conductivity measurements is shown in Figure 1. A cylindrical pellet with unknown thermal conductivity was placed between a heater at one end and a reference material, Pyrex 7740, with known thermal conductivity (8), at the other end. The hot source was made with a Pt disc and was warmed by a heating element in a stainless steel block with a peripheral guard shield to assure uniform heat flow. The metal block was kept at a constant temperature by controlling a direct current supplied to the main heater using the thermocouple and a temperature controller "EOMEGA." The platinum disc and the metal block were called the "heat" sink. A second platinum disc on top of the sample was called the "cold" sink. A small force was applied to the top of the column to simultaneously improve the connectivity between the pellets and to reduce the radiation processes.

EERC# ES08113

Figure 1. Scheme of thermal and electrical conductivity apparatus.

The thickness and the area of the coal ash specimens were 0.4–0.5 cm and 1.8–1.9 cm², respectively. The platinum discs and Pyrex 7740 had the same area, and thicknesses were 0.254 and 0.325 cm, respectively.

In order to get correct temperature measurements and to minimize the error, the Pt-PtRh thermocouples were made with fine wires (fabrication diameters of 0.1 mm). The temperatures were recorded from the central zones.

To prevent radial heat losses, two guard cylinders were used. An inside cylinder surrounding the specimen was made with Zircar® commercials available ceramic material and located around the heater and samples. The outside cylinder was a mullite tube. The ratio of the inside guard cylinder to the specimen radius was 2.0. Additionally, the space between the inside guard shield and the specimen was filled by bubbled alumina which had a low thermal conductivity coefficient (5). This reduced heat losses resulting from the convection process.

1.3 Experimental Procedure

1.3.1 Measurements of Thermal Conductivity

Five Pt-PtRh thermocouples were arranged to measure and to regulate the temperatures: T_1 recorded the temperature of the heater (first platinum disc) at the bottom of a sample; T_2 recorded the temperature between the reference sample and the Pt disc, T_3 recorded the temperature between the reference sample and the coal ash sample, and T_4 recorded the temperature of the cold sink.

To evaluate the accuracy of the recorded temperature, the temperature on Pt/Pyrex/Pt sandwich specimens was measured using two fine-wire thermocouples at each interface. The precision of the measured temperature was $\pm 0.05^\circ\text{C}$.

For temperature measurements, a Fluke Hydra 2620A data acquisition unit was used. The direct current in the heating element, the switching mechanism for reading temperatures, and the "beaded" thermocouples have shown that the reproducibility of measuring temperatures on Pt discs is superior, with absolute error $\pm 0.6^\circ\text{C}$ in the temperature range of $100^\circ\text{--}500^\circ\text{C}$.

Tests on all specimens were run for a fixed time (usually 5 min), and the outputs at that time were recorded until equilibrium was achieved. Figure 2 shows the variation of thermal conductivity with time, recorded at the heater temperatures of 125° , 415° , and 480°C for Beulah coal ash sintered at 1100°C for 3 h in air. We have developed a computer program which allows us to control and record all of the results, saving them to disc.

All test were run on well-polished pellets, previously sintered in an air atmosphere at appropriate temperatures and times, to assure good surface contact. Pellets with any flaws were rejected from further tests.

As mentioned above, Pyrex 7740 was selected as a reference material since its conduction area matched those in coal ash deposits well. Pyrex conductivity was, in turn, controlled using a specimen of fused silica. The accuracy of the thermal conductivity of Pyrex 7740 was compared with that cited in literature and was about 5%. Figure 3 shows the variation of thermal

Figure 2. Variation of thermal conductivity with time in Beulah coal ash sintered at 1100°C for 3 h. Measurements were taken at heater temperatures of 135°, 415°, and 480°C.

Figure 3. Calibration curve of Pyrex 7740.

conductivity with temperature for several runs in the temperature range of 50°-400°C, determined in our experiment and compared with those in literature (4).

1.3.2 Measurements of Electrical Conductivity

Electrical resistivity was determined separately, in the same apparatus, on the same coal ash samples, without a reference sample, and as a function of temperature using a Hewlet Packard model 3478A multimeter. This allowed us to calculate the electrical conductivity to compare that with the thermal conductivity of the coal ashes. The results of electrical conductivity variation with temperature for Pyrex 7740 are shown in Figure 3. Also, the ratio of electrical and thermal conductivities is shown in Figure 3.

1.3.3 Determination of Chemical and Mineralogical Compositions

The chemical and mineralogical compositions of the tested coal ashes were determined by x-ray fluorescence and x-ray diffraction techniques, respectively.

1.3.4 Measurements of Porosity

The porosity of sintered samples was estimated after measuring thermal and electrical conductivities using the automated image analysis of backscattered electron images. Also, closed porosity was evaluated for selected coal ashes from the weight gain of the samples after they were kept in anhydrous methanol for 24 hours.

1.3.5 Density Measurements

Densities were determined from the displacement of anhydrous methanol at room temperature using a pycnometric method with an accuracy of $\pm 0.02 \text{ g/cm}^3$. Duplicate samples were used in the experiments, and average values are presented.

1.4 **Materials**

Since thermal conductivity is very sensitive to the inhomogeneity of chemical and mineralogical compositions, a special processing technique was developed. Homogeneous amorphous coal ashes were prepared by melting at 1500°C, homogenatizing at that temperature for 3 h, and quenching at room temperature (Table 1). The glass was ground to -30 mesh and sintered at the appropriate temperature for the design time. Before sintering, all samples were in amorphous form; however, after sintering, some crystallized phases were detected. The mineralogical composition of the tested samples is listed in Table 2. Unfortunately, we were unable to determine the quantity of amorphous phase left in the samples after sintering, particularly in the grain boundaries.

Also, model sodium silicate glass and gehlenite, with the chemical compositions listed in Table 1, were used. They were prepared from oxides/carbonates by melting at 1500°C, homogenizing at that temperature, and quenching at room temperature. Before sintering, the glass was ground to -38 mesh.

TABLE 1

Composition of Beulah Coal Ash and Model Glass									
Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅
Beulah	30.1	16.2	12.3	1.7	23.8	7.2	7.4	0.1	1.2
Gascoyne	35.2	11.5	8.8	1.5	27.6	7.5	6.7	0.1	1.0
Illinois #6	50.7	18.7	21.3	0.7	5.3	0.8	0.6	1.8	0.1
Glass	61.7	14.9	--	--	11.9	1.9	9.5	--	--
Gehlenite	19.9	10.7	5.9	--	57.8	3.8	0.5	--	--

TABLE 2

Mineralogical Composition of Sintered Coal Ashes		
Coal Ash	Treatment	Major Phases
Beulah	900°C/3 h	Nepheline (NaAlSiO ₄) Gehlenite (Ca ₂ Al ₂ SiO ₇)
	1000°C/3 h	Gehlenite
	1100°C/3 h	Gehlenite
	1100°C/20 h	Gehlenite
		Häüyne ([Na,Ca] ₈ [Al ₂ Si ₂ O ₂₄][SO ₄] ₂)
Gascoyne	1100°C/15 h	Gehlenite
		Merwinite (Ca ₃ Mg[SiO ₄] ₂)
		Ferrite Spinel (Mg[Al,Fe] ₂ O ₄)
Illinois #6	1100°C/15 h	Anorthite (CaAl ₂ Si ₂ O ₈)
		Hematite (Fe ₂ O ₃)
Gehlenite	1300°C/3 and 5 h	Gehlenite

1.5 Method of Calculation

The heat flow between two isothermal surfaces and heat losses due to radiation were assumed to be the same in all experiments. This assumption allowed the determination of the thermal conductivity coefficients for unknown materials, with the same range of error.

Under such ideal conditions, the thermal conductivity coefficient of the sample was calculated from the following equation:

$$k_s = k_{ref} S_{ref} (\Delta T/x)_{ref} / S_s (\Delta T/x)_s \quad [Wm^{-1} K^{-1}] \quad [Eq. 2]$$

where k_s and k_{ref} are the thermal conductivities of the specimen and reference material, respectively; S_s and S_{ref} are surfaces of the specimen and reference material, respectively; and x_s and x_{ref} are appropriate lengths.

Electrical conductivity, $\Omega^{-1}\text{m}$, was calculated separately from resistivity results.

1.6 Results and Discussion

1.6.1 Thermal and Electrical Conductivities of Selected Coal Ashes and Model Silicates

Generally, the thermal and electrical conductivities increase with temperature and are dependent both on the chemical and mineralogical compositions (Figures 4-8). Thermal and electrical conductivities results presented on all figures correspond to those measured at equilibrium. Also, calculations of thermal conductivities of amorphous forms of coal ashes are included in the figures. Usually they are lower than those measured on crystalline forms. Calculations were performed by steady-state methods using factors provided by the literature (8,9) representing the contribution of individual oxides (on a weight-percent basis) at 30°C. The microporosity, as determined by automated image analysis of backscattered electron images, was lower than 4%. However, the microporosity of gehlenite sintered at 1300°C for 3 h was higher than 10%, and this corresponds with sample density of 3.039 g/cm³. Figure 9 shows the microstructure of gehlenite sintered at that temperature.

Figure 4. Thermal and electrical conductivities of Beulah coal ash sintered at 1100°C for 20 h in air.

Figure 5. Thermal and electrical conductivities of Gascoyne coal ash sintered at 1100°C for 15 h in air.

Figure 6. Thermal and electrical conductivities of Illinois #6 coal ash sintered at 1100°C for 15 h in air.

Figure 7. Thermal conductivity of model silicate glass.

Figure 8. Thermal conductivity of gehlenite sintered at 1300°C for 3 h (density 3.039 g/cm^3) and 5 h (density 3.050 g/cm^3) in air.

Figure 9. Microstructure of gehlenite sintered at 1300°C for 3 h.

The results of thermal conductivity of model silicate glass shown in (Figure 7) were compared with two selected from the literature with compositions that match as closely as possible to our specimen (10). Some discrepancy exists, however, between our results and those from the literature. Also, a discrepancy exists between the literature values of thermal conductivities, if measured as a function of temperature, on the order of 10% or higher.

Generally, heat in solids is conducted by: 1) free electrons that occur in metals and alloys at low temperatures, 2) by thermal vibrations of atoms that are observed in the stoichiometric dielectrics, 3) by free electrons and holes as well as the lattice vibration at the sufficiently high temperatures that are recorded in semiconductors, and also 4) ions in amorphous materials at high temperatures. In our case, the linear variations of both thermal and electrical conductivities suggest also that ionization of point defects related to nonstoichiometry, impurities, and dopants play some role in the thermal conductivity at intermediate and high temperatures. They create free carriers, such as electrons and holes, and the concentration increases with temperature. The electron/hole conductivity is reflected by the Arrhenius relationship: $\sigma = \sigma_0 \exp(-E/kT)$ where E is an energy of activation, and k is the Boltzmann constant. The magnitude of this electronic component of thermal conductivity is very low, since σ/k is about 10^{-6} . The ionic component in heat transfer, related to the diffusion of alkali ions, does not play any major role in this range of temperature and can be neglected. This component may occur above some critical temperature, across the surface, or through the volume of the material and is strongly dependent on the glass structure.

1.6.2 Effect of Porosity on Thermal Conductivity

Figure 10 shows the effect of porosity on the thermal conductivity of Beulah coal ash. Thermal conductivity decreases with the increase of porosity. Two kinds of pores are distinguished: large pores, and fine pores inside the large ones. The latter are likely formed from necks. Figure 11 shows the microstructure of Beulah coal ash sintered at 1100°C for 3 h. Porosity numbers in percent are listed in Table 3 that were estimated after measuring thermal conductivity.

TABLE 3

Porosity of Sintered Beulah Coal Ash

Experimental Conditions	Porosity, in %		Density g/cm ³
	Large Pores	Fine Pores	
1000°C/3 h	~15	16-17	2.57
1100°C/3 h	~15	17-20	2.54

Figure 10. Thermal conductivity of Beulah coal ash with varied porosity.

Figure 11. Microstructure of Beulah coal ash sintered at 1100°C for 3 h.

1.7 Conclusions

Thermal conductivity of coal ashes with low porosity (below 4%) depends upon the chemical and mineralogical compositions of the ash. Results of electrical conductivities imply that the electronic component cannot be neglected in consideration of the transport mechanism of heat. Thermal conductivity is significantly affected by porosity: it decreases with the increase of porosity.

2.0 FUTURE WORK

We intend to extend the temperature range up to 1000°C to measure the thermal conductivity of coal ashes with well-defined crystalline structures. The high temperature limit will depend on the stability of the reference material applied in measuring thermal conductivity. Also, we intend to employ model silicate systems derived from the mineralogical composition of coal ashes and amorphous phases to distinguish the variation of thermal conductivity with solid phases.

3.0 REFERENCES

1. Klemens, P.G. "Theory of the Thermal Conductivity of Solids," In *Thermal Conductivity*; Tye, R.P., Ed.; Academic Press: London, 1969; Vol. 1, p 2.

2. Laubitz, M.J. "Axial Heat Flow Methods of Measuring Thermal Conductivity," In *Compendium of Thermophysical Property Measurement Methods*; Maglic, K.D.; Cezairliyan, A.; Peletsky, V.E., Eds.; Plenum Press: New York, 1984; Vol. 1, pp 11-59.
3. Klarsfeld, S. "Guarded Hot Plate Method for Thermal Conductivity Measurements," In *Compendium of Thermophysical Property Measurement Methods*; Maglic, K.D.; Cezairliyan, A.; Peletsky, V.E., Eds.; Plenum Press: New York, 1984; Vol. 1, pp 169-230.
4. Viskanta, R. "Combined Conduction and Radiation in Semitransparent Substances," In *Thermal Conductivity*; Yarbrough, D.W., Ed.; Plenum Press: New York, 1988; pp 5-19.
5. "Standard Test Method for Thermal Conductivity of Solids by Means of the Guarded-Comparative-Longitudinal Heat Flow Technique," *Annual Book of ASTM Standards*; E 1225, 1987; pp 678-686.
6. Morris, R.G.; Hust, J.G. "Thermal Conductivity Measurements of Silica from 30° to 425°C," *Phys. Review* **1961**, *124*, 1426-1430.
7. Haacke, G.; Spitzer, D.P. "Method for Thermal Conductivity Measurements on Solids," *J. Sci. Instrum.* **1965**, *42*, 702-704.
8. Ractiffe, E.H. "A Survey of Most Probable Values for the Thermal Conductivities of Glasses Between About -150° and 100°C," *Glass Technol.* **1963**, *4*, 113-128.
9. Ammar M.M.; Gharib, S.A.; Halawa, M.M. "Thermal Conductivity of Silicate and Borate Glasses," *J. Amer. Ceram. Soc.* **1983**, *66*, C76-C77.
10. Touloukian, Y.S.; Powell, R.W.; Ho, C.Y.; Klemens, P.G. *Thermal Conductivity*; IFI/Plenum: New York, 1970; pp 922-931.

APPENDIX A

CALCULATION PROCEDURE OF THERMAL CONDUCTIVITY OF AMORPHOUS SILICATES

CALCULATION PROCEDURE OF THERMAL CONDUCTIVITY OF AMORPHOUS SILICATES

Calculations are based on the following equation (8,9):

$$10^3 k_{calc} (Wm^{-1} K^{-1}) = \sum f_i x_i$$

where f_i is the thermal conductivity factor for the component oxide and x_i is the weight percent of the component oxide. Table A-1 lists "f" factors for selected oxides derived from coal ash.

TABLE A-1

Factors for Calculating Thermal Conductivity at 30°C
From Amounts of Constituent Oxides in Glass

Oxide	Factor f ($Wm^{-1}K^{-1} \times 10^3$)
SiO ₂	13.33
Na ₂ O	-4.76
K ₂ O	2.17
MgO	21.73
CaO	13.06
Al ₂ O ₃	13.61
Fe ₂ O ₃	7.24
TiO ₂	-31.38

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Physical and Chemical Properties of Ashes and Slags (3.5)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-6000	5. Program/Project Start Date 4-1-86	6. Completion Date 9-30-92

[illegible][illegible]

12. Remarks

Due to the EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date <i>[Signature]</i> 7/15/22	14. Signature of DOE Reviewing Representative and Date
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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10837		2. Program/Project Title Physical and Chemical Properties of Ashes and Slags (3.5)		3. Reporting Period 4-1-92 through 8-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-88	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task 1	Thermal Conductivity:				
1.a	Thermal conductivity measurement device design study	10-31-91	10-31-91		
1.b	Completion of thermal conductivity device	3-31-92	3-31-92		
1.c	Completion of shakedown test matrix	5-31-92	6-15-92		
1.d	Completion of analysis of three selected coal ash slags	7-31-92			
Task 2	Strength Measurement:				
2.a	Purchase of strength measurement device	9-15-91	4-6-92		
2.b	Strength testing of two selected coal ash slags under various gasification atmospheres	3-31-92			
2.c	Completion of analysis and interpretation of strength data	6-30-92			
Task 3	Final Project Report	8-31-92			

3.6 Coal Science

**COAL SCIENCE
EARTH RESOURCE EVALUATION AND MANAGEMENT**

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

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COAL SCIENCE EARTH RESOURCE EVALUATION AND MANAGEMENT

1.0 GOALS AND OBJECTIVES

The general "Coal Science" objective of the Energy and Environmental Research Center (EERC) Mining and Mineral Resources Research Institute (MMRRI) is directed towards a fuller utilization of energy and associated energy-related data, currently available as published and unpublished documents, to better evaluate resource potential through a thorough knowledge and understanding of the geologic context of the resource. This objective is to be implemented through computer-based data management systems involving specific field examples. The focus of Year Three of the project is to further develop a computerized basis for evaluating North Dakota's lignite resource in a stratigraphic and paleontologic context. Specific goals include the construction of enhanced, but flexible, relatable database designs in stratigraphy, paleontology, and geochemistry and the testing of these designs through practical examples.

2.0 ACCOMPLISHMENTS

This semiannual reporting period is presented as a summary of the last year's effort in coal science earth resource evaluation and management. Thus this report represents a revised and more encompassing version of the January semiannual to be comprehensive. Research was undertaken during the last year that dealt with each of the milestone tasks. These tasks included A) reevaluation of the main and supplementary database designs, stratigraphic (e.g., *MNOS, *UNIT) and paleontologic (*LOC); B) database augmentation for counties in far western North Dakota and adjacent areas in easternmost Montana; C) assessment of geochemical database design and data gathering; and D) modification and expanded utilization of previously employed techniques and consideration of new techniques for displaying database information.

Substantial consideration was given to the effective use of existing databases. Revisions undertaken resulted from the desire to simplify the design of the database, as well as providing more easily interpreted output (primarily in the form of designs). Desired design changes were made possible, in part, because of new features available in Release 4 of Q&A® (by Symantec), the main database program utilized for database management at MMRRI. Additional changes result from greater output programming flexibility with the new Hewlett Packard Laser Jet III. Although some changes may appear to be somewhat cosmetic in nature, greater font control with the Laser Jet III provides the opportunity to alter the database design in the Q&A® Write module to produce easier-to-read and more self-explanatory field label descriptions.

Task B specifically included the augmentation of coal-related databases for Bowman and Slope Counties (B.1), Billings and Golden Valley Counties (B.2), McKenzie and Williams (B.3), and relevant adjacent areas in eastern Montana (B.4), including Roosevelt, Richland, Dawson, Wibaux, and Fallon Counties. As earlier database construction was based primarily on project-specific areas, current database augmentation has focused on providing general coverage, supplementing and upgrading areas with earlier database designs. Although this activity and approach is of some scale and detail in nature,

under such conditions the databases can be far more rigorously tested for practical use.

Database designs and data inputting were preliminarily completed for a variety of geochemical data types (Task C). Five databases were constructed to deal with descriptive and numerical information about rock geochemistry, rock mineralogy, groundwater geochemistry, coal geochemistry data, and rock lithologies. This aspect of the project was undertaken with the desire to integrate geochemically oriented data with stratigraphic and paleontologic databases to better facilitate the reconstruction of paleoenvironments and more definitive coal-related stratigraphic correlations. Unfortunately, few previous researchers have understood the value of having stratigraphically controlled samples, and thus much good geochemical data is of immediately limited value, beyond its original intent.

Task D encompassed consideration for improved data presentation of stratigraphic correlation data (D.1) and map presentation of stratigraphic data (D.2). Approaches taken include automated stratigraphic column construction with existing public domain programming substantially revised by this project. This method provides tremendous flexibility in facilitating the organization of stratigraphic data. Several hundreds of stratigraphic columns have been produced at a variety of scales for numerous purposes. Many of these columns have been correlated in various parts of the general project area, including Slope, Golden Valley, Billings, and Williams Counties, North Dakota, and Roosevelt County, Montana. Essentially all of the site-specific geological and paleontological observations have been plotted on both the large- and small-scale U.S. Geological Survey maps. Detailed plotting has been completed on 7.5-minute, 1:24,000-scale topographic quadrangles. Many coal-related observations were originally collected without regard to elevation. Plotting on large-scale topographic maps provides the opportunity, given the nature of the observations, to closely approximate the elevation of a particular observation. Such controlled information is of considerable importance in attempting to correlate and contour a variety of geological data types. In addition, most localities have also been plotted on linen-backed mosaics of 0.5° x 1°, 1:100,000 topographic quadrangles. These mosaics were constructed to best reflect the likely distribution of data for certain study areas, including 1) the Fort Union corridor of Williams and McKenzie Counties, North Dakota, and Roosevelt and Richland Counties, Montana; 2) the northern portion of the Little Missouri River, McKenzie County, Montana; 3) the main north-south drainage system of the Little Missouri River in Billings and Golden Valley Counties, North Dakota; and 4) additional natural outcrop and subsurface study areas in Slope and Bowman Counties, North Dakota.

Utilizing geological and paleontological database information in selected study areas tests the appropriateness of the database design for a number of specific applications, including organization and illustration of data for research and general publications, presentations, and for the construction of summary diagrams, tables, and slides. Ongoing analysis of database applications, through the integration of a variety of software, permits flexible but powerful access to a variety of information types for coal-bed stratigraphy, coal correlation and documentation, and coal characterization and assessment. These efforts have led to the development of a wide range of database applications within the MMRRRI. Of significance, in the development of these applications, is the recognition that databases can be designed for immediate (and possibly short-term) use to relate to larger

existing databases. The ability to design and redesign databases for whatever purpose is particularly important in our current environment where the needs and technical resources change dramatically over short periods of time. Computing systems that do not permit the flexibility to change with changing needs will ultimately require the researcher to attempt to circumvent the best-laid plans based on current dogma.

2.1 Database Management (Task A)

Overview of Database Design. Several purposes are served by effective database management. The foremost is the utilization of data in an effective manner. "Effective," however, is relative depending on goals and means of analysis available at a person's disposal. An understanding of coal resources and their litho- and chronostratigraphic context were "effectively" met 70 years ago under the goals of the time. Today's goals are different only in that we require (or want) greater precision in our assessments of resource characterization and context, which necessitates more data more rigorously controlled to serve specific purposes. Resource management is in a state of flux, in part, because the techniques of database management are undergoing a revolution for the individual user due to advances in computer technology and software development. Computer-based data management applications require flexibility (and transportability) while we take advantage of developments in off-the-shelf data acquisition, management, and display programming.

Q&A® Files. The data management program Q&A®, by Symantec, is particularly well-suited to the nature of geologic data, where 1) a wide range of information types are employed to manage closely related and disparate data types; 2) applications vary, and form and report modifications are made frequently; and 3) extended documentation is necessary to track on inputted numeric and descriptive data. The primary Q&A® "form" design is more appropriate than a "table" design employed by most other data managers. Q&A®'s ease of use in rigorously controlled applications presently outweighs its limitations in relational database management. These limitations were substantially overcome, however, by increased relational power in Version 4.0 of the program available for use during this reporting period.

Four main Q&A® databases control MMRRRI data types: 1) geologic section or observation location information (*MNOS), 2) geologic section unit descriptions (*UNIT), 3) paleontologic specimen location and stratigraphic information (*LOC), and 4) taxon identification information (*SPP). The prefix "*" denotes a specific file name, such as "WB" for Williston Basin. A number of other databases are employed to "feed" basic information to these primary databases. These secondary databases serve several useful functions in promoting control over frequently general (descriptive) information. Examples of secondary databases include EPCODES (chronostratigraphic terminology), FMCODES (lithostratigraphic terminology), COLOR (color coding, as per the Geological Society of America's Rock Color Chart (with Munsell color standards), and MAPS (U.S. Geological Survey 7.5-minute, 1:24,000-scale topographic quadrangles).

The *MNOS files contain information on the location of geologic observations, such as surface and subsurface measured sections (Appendix I). The *MNOS form contains 141 fields, representing four major types of field data: 1) reference information, including numbering systems; 2) location and landowner information; 3) litho- and chronostratigraphic information,

including section thickness and elevation data; and 4) sample and specimen information. A general review of these major field types is given in the following paragraphs. Note that a number of the following *MNOS fields are designed to use restricted-value internal lookup tables (see discussion under Q&A® file modifications).

General reference information fields (see Appendix I) contain data on the source of the information (i.e., citation), including 1) authorship and pagination; 2) project chief and institutional or agency affiliation; 3) individual, and affiliation, responsible for section interpretation; 4) name (if any) of geological observation (e.g., Tepee Buttes section); 5) type of geologic observation (e.g., surface or subsurface); 6) type of subsurface logs (e.g., gamma log); 7) whether photographs of the surface section, core, or of general location are available; and 8) the location of geologic observation in cross section panels. Reference numbering systems include 1) UND-EERC-MMRRI "M-number"; 2) reference number(s), associated with the source of information, such as a number specifically associated with the publication or in-house report of the geologic section; 3) original field number, usually referring to the original number used during field work; 4) institutional number, referring to numbering systems employed by various agencies or institutions (e.g., NDSWC 4252 = North Dakota State Water Commission Number 4252); and 5) any other number that might be applied to the observation. Record management fields, associated with basic reference information, are used to 1) code the primary or unique form for each M-number, 2) code data types, 3) note when and who entered data, 4) note if data has been changed since the last recorded input, 5) code utility fields which indicate the use of the data (e.g., NCRDS), 6) note whether the observation has been plotted on topographic maps, and 7) note how the information has been filed (for hardcopy records).

*MNOS file location fields contain information ranging in scale from general political boundaries to site-specific coordinate systems. Location fields include 1) nation, 2) state, 3) county, 4) region, 5) field area, 6) map reference (e.g., U.S. Geological Survey 7.5-minute, 1:24,000-scale topographic quadrangles and associated data), 7) township and range location, 8) footage and/or meters from section lines, 9) longitude and latitude (in decimal format or as degrees, minutes, and seconds), 10) UTM coordinates, 11) state land grid coordinates, and 12) general location comment field. *MNOS files use the MAPS file as an external lookup table to import map reference information. Fields containing distances can be entered either as English or metric units, with automatic conversions to respective fields.

*MNOS litho- and chronostratigraphic information is contained in fields that reference 1) the section thickness, 2) the elevation of the section at its top and base, 3) the geologic age of the measured section or observation, 4) the formations represented in the section, 5) the thickness of the formations represented in the section, 6) whether or not the formation is complete at this location, 7) a general listing of the named beds in the section, 8) the primary formation (used for bed-specific observations), 9) specific reference to a particular bed, 10) the original name of the bed (many bed names are revised), 11) the unit number for the bed in the geologic section, and 12) a general stratigraphic comment field. *MNOS files use the EPCODES and FMPCODES files as external lookup tables to import chrono- and lithostratigraphic reference information directly into an *MNOS database. Fields containing thicknesses can be entered either as English or metric

units, with automatic conversions to respective fields. The *MNOS form also contains fields for information on lithic and fossil samples.

The companion file to the *MNOS database is the *UNIT database (see Appendix II). Like *MNOS files, a number of *UNIT databases use fields designed for restricted-value internal lookup tables (see discussion under Q&A® file modifications). *UNIT files have 77 fields specific to the reference, measurement, and description of a unit (or bed) in a geologic section. A "unit" is a stratigraphic interval, identified by the geologist, that is sufficiently distinct from lithologies above and below to represent a discrete portion of the overall geologic section. *UNIT databases can be related to *MNOS databases through the creation of derived fields in the Report Module of Q&A®, thus expanding the capability of sorting *UNIT files on additional reference and location information.

Reference fields include general citation data, MMRRRI M-number numbering system, and record management fields. General location information for easy reference purposes is also provided in state and region fields.

The majority of the *UNIT fields concern the naming, measurement, and description of unit data. The unit (bed) name and formational assignment is given also with necessary comments on revised lithostratigraphy. The unit thickness can be directly inputted in English (including nondecimal entries) or metric units, with automatic conversion to respective fields, or the thickness can be calculated from scaled measurements taken from drawings or photographs. Unit thickness can also be calculated from original structural data (e.g., pace and compass method) associated with the measurement of either the unit itself or section in which it is found (SECTION STRUCTURAL INFORMATION).

The unit (or bed) description can be quoted in full from the original source (REF), and can be separated into its component parts to permit uniform interpretation and sorting on specific data types. Standard lithic field types include 1) primary rock type, 2) rock-type modifiers, 3) fresh and dry colors (GSA rock color chart), 4) sedimentary structures, 5) grain size sequencing, 6) weathering profile, 7) interpretation of the sedimentary depositional environment, and 8) interpretation of fossil-indicated environment. *UNIT files use the COLOR and STRATCOL/STRATA files as external lookup tables to import color values, and graphic and weathering symbol codes directly into a *UNIT database.

Other fields manage information to provide uniform coding procedures for specific projects (e.g., NCRDS data fields) or computer programs (e.g., STRATCOL/STRATA). For example, the *UNIT database is designed to generate reports for the program STRATCOL/STRATA. With only minor modifications, these files can be directly read by STRATCOL/STRATA, thus quickly producing a graphic representation of the geologic unit.

*LOC files contain records on the location of fossil localities and is specifically designed for micro- and macrofossil specimens (see Appendix III). The *LOC file is similar to *MNOS files in general design, containing the nearly the same fields for reference and location data. Like the *MNOS form design, *LOC files contain a number of coding fields that are used for sort routines of age-related information and uses the MAPS file as an external lookup table for map reference information. Also like *MNOS databases, *LOC

databases use fields designed with restricted-value internal lookup tables (see discussion under Q&A® file modifications). *LOC files contain 138 fields organized into the following major field types: 1) reference information, including numbering systems; 2) location systems, including elevation data; 3) litho- and chronostratigraphic information; and 4) paleontologic data. A general review of these major field types is given in the following paragraphs.

Specialized reference information includes the following record management fields: 1) unique L-number (UNQ), 2) field trip code (FY), and 3) fossil category code (FS). The unique L-number field is a combination of the L-number and the primary form field (P) and is inputted automatically. This unique number permits other databases (e.g., *SPP) to construct derived fields utilizing *LOC locality and stratigraphy data. The field trip code provides an additional means of sorting locality data on the basis of when the information was taken. The importance of this field is that it permits sorting across project categories and data entries in different field books. The fossil category code permits a retrieval and sort on a selected major taxonomic category. For example, a retrieval could be made on only microfossils from any of the stratigraphic or location fields in the *LOC database.

The *LOC database stratigraphically oriented fields differ from *MNOS databases in that fields are designed to permit precise reference of a fossil locality to an intra- or extraformational stratigraphic marker or horizon. In addition, a locality can be placed in reference to the base or top of the enclosing formation. Various code fields document the predicted error associated with the placement of a locality relative to any of these horizons. Besides these "relative" stratigraphic fields, the elevation of a locality, and its interpreted error, can also be inputted. All of these fields can be entered in either English or metric units, with automatic conversion to respective fields.

Additional stratigraphic field types include 1) the formation and member to which the locality can be assigned, 2) the general level of the locality within the formation (e.g., upper, top), 3) the original formation used by the discoverer of the locality, 4) the measured section and unit numbers (i.e., *MNOS and *UNIT) to which the locality belongs, 5) the age of the locality (i.e., Tiffanian Stage), and 6) an extended comment field for additional stratigraphic considerations. As with the purpose of similar general fields, the reference source can be quoted (at length) to document the exact meaning of the original author.

*LOC database fields specific to paleontology are primarily concerned with the record of fossil discovery, collection, and identification. These topics are covered in the following fields: 1) discoverer(s), date of discovery, and comments on how the discovery occurred; 2) field crew chief and affiliation; 3) collector(s), date of collection, and comments on the contributions of the collectors; 4) the collection repository and comments on the quality (preservation) of the collections; 5) faunal comments on the assemblage of fossils collected and their significance; and 6) a list of the fossils identified, and the name (and year) of the person responsible for their identification. The *SPP database is a companion to *LOC files and records detailed information on the identification of taxa from a particular locality. The *SPP database can be used as an external lookup table to

combine taxon identifications with stratigraphic and location data. Although not discussed at length in this report, the following field types constitute the *SPP database: 1) taxon identification, 2) a simplified classification of the taxon, 3) repository and specimen numbers, 4) number of specimens, and 5) identification comments. Both old and revised identifications are recorded to provide a history of study on specific specimens and taxon names. *SPP uses the database MCLASS as an external lookup table to extract classification data. With *SPP, *LOC, and MCLASS data bases, the stratigraphic range of taxa can be determined through a merge of the data from the three files.

Q&A® File Modifications. A number of database design modifications were anticipated and were produced as a result of the Release 4 of Q&A®. Some of the form design differences, compared to previous reports (Hartman, 1990b, 1991a, 1992a), are evident in the new designs of the databases themselves, as can be examined in Appendices I (*MNOS), II (*UNIT), and III (*LOC). However, substantial changes were also made in the functioning of the geological and paleontological databases, as it pertains to the File, Report, and Write modules of Q&A®. Important program features include 1) extended relational data management capabilities; 2) extended programming language; 3) increased (effectively unlimited) field length, with the capability of designing forms with portions of lengthy entries "hidden," which permits a more streamlined database design; and 4) the ability to select data for database entry from prescribed internal and external databases (lookup) tables. Important secondary features include 1) word-processing capabilities in the file module (e.g., within a given field), 2) spell-checking in the file module, 3) the ability to change field names (Set Field Names) for the purposes of programming and designing new forms in the Write module, 4) expanded macro program facilities, 5) new export and import capabilities with other database managers, 6) greater font control in the various modules, and 7) a new compression backup utility. Although the physical appearance of the database design has, in some ways, changed substantially, these changes are a natural outgrowth of the functionality and basic purpose of the earlier designs.

The results of these module improvements can be seen in 1) the additional ease in which data can be entered through copy and insert file functions in the update mode in the File module; 2) the enhanced ability to restrict data entry, reducing, if not eliminating, incorrect input (see below); 3) substantially fewer errors in the entry of information in comment-type fields (e.g., LOC, STRAT, FAUNAL, COM) as a function of a spell-check facility; 4) increased flexibility to redesign and program databases with editing functions in the design and program modes of the File and Write modules; and 5) the ability to control database form design in the Write module with the use of scalable fonts tied to absolute ("real") tab settings. Of particular importance is the upgraded ability to import data (from other databases) to serve as a lookup file for data entry. Through a specific function key combination, a lookup window appears over the database form, from which the appropriate entry can be selected and automatically inputted in the database. Along with custom-designed help-lookup windows, editing time and quality of the inputted data are substantially reduced and improved, respectively. With the more refined control of scalable fonts, the *MNOS, *UNIT, and *LOC databases were redesigned (see relevant appendixes). These changes, which are in part cosmetic in nature, permit some additional database design refinements through the ability to precisely select the needed point size. As a result, most field names in database forms produced using the Write module can be written in full, reducing the number of somewhat cryptic

field labels. In addition, extended comment fields require substantially less space with the use of proportional fonts.

Selected Q&A® database modifications include the following programming statements: 1) a check for the existence of a primary form between *UNITS and *MNOS databases, 2) a comparison of identical quadrangle names (in an *MNOS or *LOC database) found in more than one state in the MAP database, 3) a thickness value comparison between the related *MNOS and *UNIT databases, and 4) an approximation of quarter sections derived from original footages from a section. The first three programming statements provide safeguards or checks on appropriate inputting between related databases. As an example, a U.S. Geological Survey topographic quadrangle name is unique to a state, but may be used in another state (e.g., the map name Black Butte is used both in North Dakota and Montana). Because each map name must be unique in a database for accurate external lookups, a map name must be modified by adding the state abbreviation (e.g., "Black Butte (ND)"). A person that is inputting a map name is not expected to know which map names are in common between states, so the program routine prompts the inputter with an appropriate choice. The last programming statement, mentioned above (no. 4), is used to aid in plotting of geographic locations on varying scale maps (particularly 1:100,000). The approximation of a quarter-quarter section permits a quick method for placing a location on a small-scale map. The conversion from a footage given location to a legal location is completed automatically.

Besides the *MNOS, *UNIT, and *LOC file modifications mentioned above, database "form" design modifications were made to a number of Write module output forms. Also, a new database, SPEC, was constructed for the purpose of controlling data associated with collected samples and for printing collection labels. The greater font control, available with Version 4 of Q&A®, makes possible the printing of the necessarily small form designs and associated data. Multiple copies of appropriate forms (for samples from the same location) are then easily produced in the merge-data portion of the Write module.

Design modifications were also implemented for *UNIT databases to permit the output of data in NCRDS, STRATIFACT® (by GRG), and LOGGER® (by Rockware). See Appendix II for examples of *UNIT database form design and the outputted data format (e.g., NCRDS).

2.2 Database Augmentation (Task B)

Data Input. The geologic exposures of far-western North Dakota are largely derived from the drainage patterns produced by the Little Missouri and Missouri Rivers. The relatively good outcrops along these rivers, and some of their tributaries, have been the source of many independent coal and noncoal studies. Much of this data has never been assimilated for the purposes of detailed coal correlation, and is, for the most part, not part of any database system.

As part of this Coal Science database design and management program, Williston Basin stratigraphic data were cataloged and computerized from data sources relevant to exposures along the Little Missouri and Missouri Rivers in western North Dakota, and adjacent areas in the drainage of the Yellowstone and Missouri Rivers in eastern Montana. Input study areas in North Dakota included 1) Bowman and Slope Counties, 2) Billings and Golden Valley Counties,

and 3) McKenzie and Williams Counties. These county-based areas represent, to a certain extent, well-defined input data sets, based on the nature of available outcrops and county surface and subsurface studies. The input coverage in the adjacent counties in Montana is less comprehensive, which simply reflects project goals focused in North Dakota. Coverage in Montana included Roosevelt, Richland, Dawson, Wibaux, and Fallon Counties. The stratigraphic data inputted for North Dakota represents primarily the Fort Union Group, which includes the Ludlow, Cannonball, Slope (upper Ludlow of some authors), Bullion Creek (= Tongue River in adjacent Montana), and Sentinel Butte Formations. To date, the following M-number geological observations have been recorded in North Dakota: 1) 609 in Bowman County, 2) 49 in Adams County, 3) 1664 in Slope County, 4) 63 in Hettinger County, 5) 421 in Golden Valley County, 6) 344 in Billings County, 7) 171 in McKenzie County, and 8) 199 in Williams County. In Montana, M-number geological observations have been inputted as follows: 1) 64 in Roosevelt County, 2) 72 in Richland County, 3) 146 in Dawson County, 4) 110 in Wibaux County, and 5) 56 in Fallon County. As part of this research, an annotated bibliography of unpublished and published coal-related observations has been compiled to facilitate computerization (Appendix VI). Publications included in the last reporting period include (See Appendix VI bibliography) Anna (1980), Archibald (1982), Benson (1953), Bluemle (1971), Carlson (1973), Denson and others (1959), Fisher (1954), Flores and Lepp (1983), Gregory Drilling, Inc. (unpublished drilling logs), Hartman (1991 unpublished field notes), Jacob (1976), Kroeger (1988 unpublished field notes), Pipiringos and others (1965), Steiner (1978), Stevenson (1956), and U.S. Geological Survey Open-File Report 76-888. Some geologic data was also previously entered for stratigraphic studies of relevant comparable summary sections in the coal-bearing strata of Harding County, South Dakota.

During January-May, effort was been extended to produce a paper-based "library" of computerized data. This entails assembling the original published and unpublished source of the M-numbered sections (*MNOS database) and ordering them in a set of ring binders for archival purposes. Although this compilation has been ongoing, an attempt was made to bring the catalog up to date, which involves the copying of thousands of records. An archived "hard copy" system provides a permanent method of verifying the use of the M-number assigned to a particular geological observation. The process of back-logging previously M-number geological observations is effectively complete for current considerations.

Stratigraphic and paleontologic data were also computerized for studies in the Bighorn Basin of northwestern Wyoming and south-central Montana. This work is directed towards establishing nonmarine molluscan criteria for recognizing Clarkforkian (Paleocene)-age strata in the Williston and Powder River Basins. This interval represents important coal-bearing sequences in the upper part of the Tongue River Member of the Fort Union Formation and in the lower part of the Wasatch Formation in the Powder River Basin. This time interval cannot be precisely correlated into the stratigraphic section of the Williston Basin, but must, in part, be correlative with the Sentinel Butte and Golden Valley Formations.

Stratigraphic and paleontologic data were also computerized for the Powder River Basin of northeastern Wyoming and southeastern Montana. This data will augment substantially the database previously compiled for the temporal control of coal-bed correlations in the basin (Hartman, 1990a,

1992d). At present, approximately 300 nonmarine molluscan localities have been used to chronostratigraphically organize the coal beds of the Powder River Basin. Newly available unpublished data will approximately double this number of localities, increasing the number of new control points, probably by about 30 to 50 percent.

Additional unpublished stratigraphic coal-based data was acquired for a number of areas in the Williston Basin in Montana and North Dakota through the courtesy of Mr. John Spencer of the Billings office of the Bureau of Land Management. This material was produced by the U.S. Geological Survey, primarily for the purposes of coal land classification and was never published or open-filed. Areas of study represented by these data include 1) the Yellowstone and Missouri River confluence area of Montana and North Dakota (including the Culbertson and Girard coal fields, and route of a portion of the northern tier pipeline); 2) the Nesson coal field of Williams and McKenzie Counties; and 3) the Jordan coal field of Garfield County, Montana. Selected geologic and paleontologic data of the Jordan coal field were incorporated in studies on the biostratigraphy of the Hell Creek/Tullock Formation transition in Garfield and McCone Counties, Montana (Hartman, 1991b).

Additional database augmentation incorporated unpublished, computerized, coal-related databases constructed by LeFever and Murphy (1983) in a project entitled "Mining Resources and Potential Problems Associated with Mining of Cenozoic Rocks of the Williston and Powder River Basins, Northern Great Plains." These databases have not been utilized since their compilation. They were constructed on an IBM mainframe computer utilizing the program system SAS (SAS Institute, Inc.) before the advent of powerful microcomputers. Downloading these files, from an old version of SAS, proved to be tedious, and exemplifies the need for data to be stored in a manner that permits their transfer between computing systems. All of the files from the LeFever and Murphy (1983) project were downloaded as ASCII files and subsequently inputted into Q&A® databases. Additional effort will be required to decode data originally encrypted to circumvent storage and line length limitations imposed on the IBM system. When completely upgraded, the LeFever and Murphy (1983) files will be imported into the Williston Basin MNOS database. Incorporation of these data into currently maintained databases will provide an excellent opportunity to test present database designs.

Video Imaging. The video imaging of small but macrofossil-size specimens was undertaken for the purposes of morphometric analysis and illustrations for presentations. The video imaging system has been used extensively in the studies of Mr. Timothy J. Kroeger for micro-sized palynomorph samples, and in this writer's studies of small, macro-sized bivalves and snails. Morphometric techniques developed utilizing this system provide considerable additional rigor in discriminating between taxa of mollusks. This ability thus enhances the opportunity for highly resolved interpretation of time through coal bed sequences to interpret their environmental history. Numeric data derived from these studies are maintained in Q&A® databases and Quattro Pro® spreadsheets.

Recent video-imaging considerations to enhance sample image quality have focused on an attempt to implement greater gray-scale control to improve resolution. A meeting with a representative of Leeds Precision Instruments resulted in the purchase of software capable of externally controlling the gray scale range (gain and offset) of the system's Cohu camera outside of the

environment of the video imaging software. Software acquired from Computer Imaging Applications significantly improved gray scale control thus affording an improved image for video capture.

This writer attended a "Video Imaging and Analysis Seminar" sponsored by Leeds Precision Instruments. Presenters included the manufactures of the hardware and software utilized in Coal Science projects. As a consequence of these meetings, and previous considerations as to the needs of ongoing data management and project needs, new hardware and software was ordered to upgrade the current operating system to a Microsoft Windows environment. The hardware order represents an upgrade to the CFG VisionPlus-AT framegrabber by Imaging Technology, Inc. This board will permit greater resolution without loss of overlay capabilities used in more sophisticated video capture programs and applications. The software order is an upgrade to the video capture program Optimas by Bioscan. Besides its enhanced analytic capabilities, Optimas permits a far better environment to exchange captured images with other Windows graphic drivers and related programming and should permit a far wider range of data management applications.

2.3 Geochemical Database Design (Task C)

In the context of the present Coal Science program, the purpose of designing a coal geochemical database, or any other similar analysis-type database, is to place such observations in a geologic framework. Thus geochemically oriented data can be integrated with stratigraphic and paleontologic databases to better facilitate the reconstruction of paleoenvironments and produce more definitive coal-related stratigraphic correlations. Such abilities thus afford a more comprehensive and meaningful interpretation of geologic history. Isolated coal analyses, without geologic context, have limited value in providing a means to correlate coal beds and coal-forming environments or to interpret depositional or diagenetic histories.

For the purposes of present database considerations, coal and rock geochemical data was downloaded from a mainframe database constructed for another project by LeFever and Murphy (1983). This data set was chosen because it was originally constructed for the purpose of posing questions of concern to individuals in coal resource assessment. These databases incorporate standard analytical data (e.g., Btu value, sulfur content, etc.) along with stratigraphic data, utilizing Q&A®, *MNOS, and *UNIT files and formats (see Appendix IV). All of the available data, representing several thousand initial observations, has been incorporated into specifically designed Q&A® databases. Unfortunately, very few chemical observations can be tied to specific stratigraphic sections, let alone their placement relative to specific horizons. The use of the LeFever and Murphy (1983) database clearly illustrates the problems attendant in the taking, recording (in the field), and tracking of geochemical data by earlier coal-oriented projects. A very low percentage of the "coal geochemistry" data can be specifically tied to a specific coal bed or even to a specific point on the ground. Thus, much good geochemical data is of immediately limited value, beyond its original intent. Appendix IV provides a detailed account of the geographic, geologic, bibliographic, lithologic, and coal chemistry data given by LeFever and Murphy (1983). As noted, all of their data has been inputted into specially designed Q&A® databases. These databases are related to one another through unique locality numbers.

2.4 Data Presentation (Task D)

Display of information in maintained databases is an important aspect of database utilization for the research scientist. Database management programs, such as Q&A®, provide a means to show data in various output formats. Data is most commonly displayed in tables, as rows and columns of observations, or as forms, depending on the nature of the intended use. In addition, graphical representation of data is particularly important where data is inherently visual (e.g., geologic sections) or numeric (e.g., analyses). Of considerable importance to data visualization is the ease with which the data can be displayed. The visualization of data should be used as a tool in data analysis and not an end in itself. The more easily data can be viewed, the more likely it will be used as a tool to permit the researcher to make better interpretations.

The program STRATCOL/STRATA (derived from a public domain program by Peter Guth) produces a graphic presentation of geologic logs from *UNIT databases. Through the use of Q&A® and STRATCOL/STRATA, a graphic representation of a geologic column can be produced with a laser printer in a matter of a few minutes. Additions to the *MNOS and *UNIT files also include entries specific to STRATCOL/STRATA (see Appendix II). Thus any geologic section inputted into the *UNIT database can be conveniently graphically represented for research studies.

A *MNOS base map reference system was initiated during Year Two of the Coal Science project and continues to be used for the plotting of the location of geologic observations. This system employs U.S. Geological Survey 1:24,000- and 1:100,000-scale maps. Surface and subsurface sections are plotted on the 1:24,000-scale maps with as much precision as is available. Elevations of the top and bottom of surface sections are compared with original data, or a "best fit" is determined if elevation data is not available. Paleontological observations are similarly plotted on the same maps. These maps will be used as the basis for digitizing coal and related geological observations for use in geographic information system programming and geologic software. In addition, *MNOS data is also plotted on a set of linen-backed topographic 1:100,000-scale maps. These maps have been put together to form a mosaic of far-western North Dakota and easternmost Montana. Essentially all of the M-number and L-numbered localities housed in Coal Science databases for easternmost Montana and far-western North Dakota have been plotted on 1:24,000 and 1:100,000-scale maps.

2.5 Database Implementation

Implementation or utilization of a database is the best means to realize the requirements for its effective use. The databases so far constructed and augmented have been used in research projects that test database design. These projects are discussed in the following section.

Research Studies. Field, laboratory, and computer-based activities have greatly facilitated the diverse requirements for the construction of database systems that can be used as a tool in research, rather than as a means to gather data. The following section represents studies undertaken with the purpose to fully test and implement databases constructed under the Coal Science program. To indicate the continuity of these studies, as part of the

overall approach to this report, most of the research studies undertaken during the 1991-1992 fiscal year have been included.

Abstracts previously submitted for publication were presented to the Geological Society of America (GSA) and Society of Vertebrate Paleontology (SVP) for presentations at their annual meetings in San Diego in October. The GSA abstract summarizes research conducted on the stratigraphy and molluscan paleontology across the Cretaceous-Paleocene boundary in the northern Great Plains (Hartman, 1991b). Information utilized in the preparation of this paper was derived from databases maintained in Q&A® for the Williston, Powder River, and Crazy Mountains Basins in the northern Great Plains of the United States and Canada. The abstract delimits the occurrence of certain taxa through the uppermost Cretaceous Hell Creek and Lance Formations and Paleocene Ludlow, Tullock, and Bear Formations, providing biochronologic control for temporal correlations across North Dakota, Montana, Wyoming, and Saskatchewan. This abstract was submitted by invitation for a theme session on the "Fossil Record at the Cretaceous-Tertiary Boundary."

The SVP abstract summarizes research conducted on the stratigraphy and mammalian and molluscan paleontology of the Paleocene Sentinel Butte Formation in the North Dakota portion of the Williston Basin (Kihm and Hartman, 1991). Field work conducted over the last two summers relocated all of the previously known mammalian localities and rigorously defined their geographic and stratigraphic positions. These data were substantially revised from previously published reports. The coal-bearing strata of this formation can be shown to be somewhat older than previously considered, and is equivalent in age to the important coal-bearing sequence of the Tongue River Member of the Fort Union Formation in the Powder River Basin of northeastern Wyoming and southeastern Montana. All data associated with this effort, including both historic and modern stratigraphic and paleontologic observations, were maintained in databases designed under the Coal Science program.

A paper submitted for publication was presented as a poster session with Dr. Allen J. Kihm, in October, at the Sixth International Williston Basin Symposium (and Fourth Saskatchewan Petroleum Conference) in Regina, Saskatchewan. This paper concerns the stratigraphic and biochronologic context of pantodonts (vertebrates) in North Dakota. By more rigorously defining the stratigraphic and geographic position of a number of localities, the stratigraphic distribution of this group has been shown to be more temporally restricted than previously understood. This type of information permits more precise temporal (biochronologic) correlation of the coal-bearing strata of the upper Bullion Creek (Tongue River) and Sentinel Butte Formations. All of the stratigraphic and paleontologic data used to construct this paper, and associated figures, was organized through Q&A® databases developed and tested through Coal Science field and laboratory research.

Research was undertaken on the freshwater and terrestrial molluscan fauna of the Riverdale Locality, on the eastern bank of Lake Sakakawea, McLean County, North Dakota. Previously collected snails were curated for the purposes of morphometric and photographic study. The terrestrial snails, so far processed, were examined by Dr. Barry Roth, a consulting paleontologist from San Francisco, California. This material, along with the freshwater taxa, will form the basis of a publication on the most diverse nonmarine faunule of the Paleocene in North Dakota, and possibly in North America.

A Symposium on the *Paleontology in North Dakota: Fossils as a Resource in Research, Education, and Economics* was held April 30th at the 84th annual meeting of the North Dakota Academy of Science (Hartman, 1992b, c). This symposium was convened by Dr. Allen J. Kihm of Minot State University and this writer to provide a public forum for relating matters of statewide concern in regards to the fossil resources of the state (Hartman and Kihm, 1992). Nine presentations were given encompassing the entire exposed bedrock and Quaternary fossil fauna and flora of North Dakota. The presentations were followed by a group discussion in which the more than 50 people who attended the symposium participated. The symposium was covered by the Grand Forks Herald and the Associated Press wire service. Preparations for this event included mailings to various federal and state agencies and committee representatives.

Collaborative research, undertaken with Dr. David Krause of the State University of New York at Stony Brook, has resulted initially in the acceptance of an abstract to the annual meeting of the Society of Vertebrate Paleontology (Krause, et al., in press, 1992) on the "Latest Cretaceous and early Paleocene mammals from Makoshika State Park, Williston Basin, eastern Montana." This study, representing one of a number of site-based projects, is on the vertebrate paleontology and stratigraphy of Makoshika State Park, Dawson County, Montana. This research specifically pertains to the early Paleocene Hiatt Locality, which was discovered by Dr. Robert Hiatt, of Glendive, many years ago. The value of this research is in that temporal data is being documented for the base of the coal-bearing sequence in an area of the Fort Union Lignite Region where no such data was previously available. Such information bears on developing an understanding of the chronology of the Cretaceous/Tertiary transition, representing a shift in paleoenvironments from noncoal to coal-dominated settings. This research ties in directly with studies underway in southwestern North Dakota by Kroeger (dissertation project mentioned below), Hartman and Cvancara (in preparation, 1992), and Hartman and Krause (in preparation), in the western Williston Basin of Garfield and McCone Counties, Montana, by Hartman (1991a, 1992d) and Hartman and Rolland (in preparation), and in the Crazy Mountains Basin of Sweet Grass and Wheatland Counties, Montana, by studies of Hartman, Krause and others.

Samples of North Dakota tuffs, collected by Dr. Nels Forsmen of the University of North Dakota Department of Geology and Geological Engineering, were sent for age and geochemical analysis. One tuff, referred to as the Marmarth tuff, is from uppermost Cretaceous strata in southwestern North Dakota. The other tuff is the well known (but poorly documented) "blue bed" of McKenzie County, North Dakota. The tuffs will be age dated by Dr. Carl Swischer of the Institute of Human Origins. Very few isotopic dates are known for bedrock North Dakota strata. This information will place the section of strata represented between these two tuffs in an entirely new context permitting continental and global scale comparisons of previous continental configurations hypothesized for this interval. These analyses will be paid for by Dr. Malcolm C. McKenna of the American Museum of Natural History. Dr. George Shaw, of Union College, Schenectady, New York, will use an inductively-coupled plasma quadrupole mass spectrometer to fingerprint the tuffs for future lithostratigraphic correlation projects to fully utilize the poorly known volcanic record as preserved in North Dakota.

Research has commenced to published the stratigraphic distribution of historically important fossil mollusk localities in the coal-bearing strata of

the Upper Cretaceous Fruitland and Kirtland Formations on various mine leases in the western portion of the San Juan Basin in northwestern New Mexico and southwestern Colorado. The field research undertaken for this project was supported by the New Mexico Bureau of Mines and Mineral Resources. Data analysis extensively utilizes databases constructed for Q&A® *MNOS, *UNIT, and *LOC databases. Although undertaken separately, this work will provide needed context for interpreting the biostratigraphic range of Upper Cretaceous molluscan taxa elsewhere in the western interior of North America. Results of this research will form the basis for systematic studies undertaken by Ms. Rolland mentioned below.

At the end of June and in early July, the results of stratigraphic and paleontologic studies on the "Biochronology of uppermost Cretaceous and lower Tertiary nonmarine Mollusca of the northern Great Plains, U.S.A. and Canada" were presented at the Fifth North American Paleontological Convention held in Chicago (Hartman, 1992d). The convention is held every four years, and on this occasion was attended by over 500 paleontologists from around the world.

Field Research. Field research represents the applied connection between data gathering, its management, and subsequent implementation and revision. A utilitarian database design is forged through use having specific goals and applications. The field research and database implementation discussed below have resulted in significant improvements in the approach to database management. Field research undertaken during the last summer field season was fully summarized in a previous technical report (Hartman, 1992a).

Field work recently undertaken includes the study of fossils and strata of the uppermost Cretaceous Hell Creek Formation of the Missouri and Little Missouri Rivers in southern North Dakota. This research concerns documenting the Hell Creek stratigraphic distribution of molluscan taxa in the North Dakota portion of the Williston Basin. Other research in the western portion of the Williston Basin in Garfield and McCone Counties, Montana (Hartman, 1991b; 1992d) has delineated the biostratigraphic ranges of most Lancia taxa known in the northern Great Plains. Studies in North Dakota provide the necessary biochronologic continuity to interpret the temporal history of the easternmost extent of Upper Cretaceous strata.

Research of T.J. Kroeger. Mr. Kroeger, a Ph.D. candidate in the University of North Dakota Department of Geology and Geological Engineering, is in the later stages of his dissertation studies entitled "Paleoecology of palynomorph assemblages in the upper Ludlow Formation (Paleocene), southwestern North Dakota." Mr. Kroeger is in the process of analyzing and interpreting the palynomorph-bearing sediment samples for brackish and marine indicators to provide greater resolution in interpreting these environments in the western Slope and southwestern Golden Valley Counties, North Dakota, and in Dawson County, Montana. In addition to his dissertation studies, his research has identified the Cretaceous-Tertiary boundary in surface and subsurface samples in Slope County, North Dakota, and in surface samples from Makoshika State Park, Dawson County, Montana. This information will be used in conjunction with age information interpreted from the nearby Hiatt mammal locality for the purposes of establishing a chronostratigraphic framework for the transition between largely nonlignite-bearing to lignite-bearing strata along the Yellowstone River and elsewhere. Mr. Kroeger's research makes extensive use of Q&A® "coal science" databases including the *MNOS and *UNIT databases, as well as other that have been specifically designed for sample

record keeping in the laboratory and as accession records into the collections of the University of North Dakota.

Research of W.D. Peck. Mr. Peck, a Master's student in the University of North Dakota Department of Geology and Geological Engineering, is in the final stages of completing his project entitled "The stratigraphy and sedimentology of the Sentinel Butte Formation (Paleocene) in south-central Williams County, North Dakota," and will defend his effort in July. As a part of current related studies, Mr. Peck, with Dr. Allen J. Kihm and this writer, has attempted to construct a coal-based correlation framework for the area between the Nesson Anticline and Fort Union. This effort utilizes the relatively numerous isolated reports of coal along the Missouri River that have been computerized into *MNOS and *UNIT databases. Aspects of our study have been incorporated into Mr. Peck's thesis research. A final thesis manuscript has been submitted to his graduate committee.

Research of M.M. Rolland. Ms. Rolland has undertaken a senior thesis project, under this writer's supervision, in the University of North Dakota Department of Geology and Geological Engineering. The project is entitled "A faunal comparison of selected freshwater mollusks from the Upper Cretaceous (Edmontian?) Fruitland Formation of the San Juan Basin, New Mexico, with the Hell Creek Formation (Lancian) of the Williston Basin, Montana-North Dakota." Ms. Rolland's study, which is being partially supported by a grant from the local chapter of Sigma Gamma Epsilon, a National Honorary Society for the Earth Sciences, involves the paleontologic and stratigraphic study of nonmarine mollusks from the coal-bearing strata of the Williston Basin of North Dakota and Montana and the San Juan Basin of New Mexico. Research will be directed towards understanding the evolutionary history of selected nonmarine molluscan taxa to provide a more rigorous biochronologic framework for the correlation and paleoenvironmental interpretation of nonmarine strata in the Upper Cretaceous strata of the western interior of the United States. Studies to date have utilized Coal Science data management systems (i.e., *LOC database) to revise geologic and paleontologic data concerning relevant strata in North Dakota. Field work undertaken in June specifically dealt with the stratigraphy and molluscan fauna of the Hell Creek Formation in Morton and Bowman Counties, North Dakota, representing the two main areas of exposures of Hell Creek strata in the state.

2.7 Other Research Travel

During the last fiscal year professional presentations and poster sessions were given in Regina, Saskatchewan (Hartman and Kihm, 1991), San Diego, California (Hartman, 1991b; Kihm and Hartman, 1991), and Chicago, Illinois (Hartman, 1992d). Other research travel for the July-December portion of the year has been previously fully summarized (Hartman, 1992a).

In addition, this writer attended the geographic information system (GIS) meetings in Bismarck, North Dakota, and Overland Park (Kansas City), Kansas. As previously noted, the map presentation and map analysis of geological and paleontological data is an important means to convey significant amounts of data conveniently to a large and varied audience. GIS represents a technology specifically designed to manage information that can input, manipulate, and analyze geographically referenced data. GIS programming represents a set of tools to organize, edit, analyze, display, and illustrate geographically referenced data. As essentially all of the

constructed "coal science" databases represent geographically referenced information, GIS technology represents a natural extension of developing extended analytical and display capabilities for earth resource characterization and evaluation. GIS as a data systems architecture or methodology is clearly developing rapidly, with a large number of state and federal government agencies promoting its use through their own programs. The meeting in Bismarck was entitled "North Dakota GIS Short Course," and was sponsored by the North Dakota Geological Survey. In Overland Park, I attended the "Mid-America GIS symposium." As part of this symposium, I participated in the short courses "Methods for data capture and data management" and "An overview of GIS hardware and software."

In June, this writer attended a "Video Imaging and Analysis Seminar" sponsored by Leeds Precision Instruments in Minneapolis. The results of this trip are summarized above under "Video Imaging."

Also in June, as part of results obtained through Coal Science data management studies, this writer was invited and presented a talk on the "Uppermost Cretaceous and Paleocene nonmarine molluscan and mammalian studies in the Williston Basin" at the dedication of the paleontological laboratory of the Pioneer Trails Museum in Bowman, North Dakota.

2.8 Computer Hardware and Software

As previously noted, during September, a Gateway 2000 486/33 computer was acquired (through other funding) and installed, and Coal Science database systems were transferred to this machine. The main benefit of the 486 computer is its larger (650 MB) hard drive. The 486/33, and the previously purchased Coal Science Gateway 2000 386/25, will serve as the main database management computers. Expanded database needs, focused primarily on additional staff involvement in data management and use, have resulted in the need for additional computers and, eventually, the means to connect (i.e., network) them. To date, two machines, a Standard 286 and Gateway 2000 386sx, are used specifically for data input. Although this system of four computers functions well, as databases become larger, a significant increase in efficiency could be achieved through a computer network. Installing a network, however, is currently beyond the scope of committed financial resources.

Also during September, a 150-MB hard drive was replaced (through other funds) on the Gateway 2000 386/25 computer. Hard drives do not appear to have a long half-life, which emphasizes the necessity of regular backups. In this totally unexpected hard drive crash, no information was lost as all of the data on the 300 MB of the 386/25 computer had been backed up on streamer cassettes using an Everex external drive backup system. Both the 486/33 and 386/25 computers use the Everex system. The 486/33 is routinely backed up on a weekly basis, while the 386/25 is backed up by database as needed. In January, the Gateway 2000 386/25 experienced enigmatic computer hard drive problems, which were only resolved with a new hard drive transfer cable. No data was lost as a result of these machine problems.

The upgrades to various programs were acquired throughout the year. These programs include Release 4.0 of Freelance Graphics® by Lotus Development Corporation, Release 4.0 of Quattro Pro® by Borland Corporation, Release 2.0 of Axum® by Trimetrix, Inc., Release 3.1 of Windows® by Microsoft, Release 1.0

of WordPerfect for Windows® by WordPerfect Corporation, QEMM 386® by Quarterdeck Office Systems, and Release 2.1 of F-Prot Antivirus by Fridrik Skulason (site license by the University of North Dakota Computer Center).

2.9 Sample Processing

Surface and subsurface lithic and micro- and macrofossil samples collected from coal-bearing strata from the Little Missouri River drainage of southwestern North Dakota, Yellowstone, and Missouri drainages of the Williston Basin in eastern Montana, and Crazy Mountains Basin of south-central Montana were processed, curated, and analyzed during the last year. The data derived from these samples have been and will be in the study of the biostratigraphy and event-lithostratigraphy for the temporal interpretation of uppermost Cretaceous Paleocene strata in the northern Great Plains.

Microfossil samples, consisting largely of pollen, spores, and dinoflagellates, largely comprise the dissertation studies of Mr. Timothy J. Kroeger (see under Database Implementation). Samples to be used for dissertation studies and related papers (e.g., Krause et al., in press, 1992) have been fully processed and are under analysis towards completion of dissertation studies in about 18 months.

Rotary mud samples derived from the 1990-1991 drilling project (holes M2187 and M2188) and other related lithic samples were cataloged and labeled for archival storage. The drill hole samples were described as part of DOE database management studies. Various samples were also analyzed for the purposes of coal correlation and paleoenvironmental interpretation (Hartman and Cvancara, in preparation, 1992). As determined through the archiving process, certain samples are subject to bacterial decay. Although the likelihood of decay was previously known, the speed and number of samples to be effected was not. To avoid this problem in the future, a small refrigerator was purchased to house the few samples likely to be effected that would be processed for palynomorph studies. Once these samples have been processed, the remaining material will be dried for archival storage.

Surface lithic and macrofossil samples were processed by Mr. Johnathan M. Campbell, an undergraduate student at the University of North Dakota, for biochronologic studies in the Crazy Mountains and Williston Basin. These efforts are directed towards the construction of a unified temporal framework for the northern Great Plains. In addition, Ms. Michelle M. Rolland has begun to process macrofossil samples from the western portion of the Williston Basin to compare the systematic validity of the biochronologic range of selected nonmarine molluscan taxa in the western interior of the United States.

3.0 SUMMARY AND CONCLUSIONS

The general Coal Science objective of the Mining and Mineral Resources Research Institute (MMRRI) is directed towards more effective use of geologic observations specific to the correlation and assessment of coal-bearing strata. The effective and efficient utilization of these observations requires streamlined but flexible user-oriented data management programs incorporating straightforward data inputting and summary data output in the form most convenient to the user. Substantial amounts of currently useful and historically invaluable geologic data bearing on the correlation of coal beds

is available for most coal-bearing areas. This is certainly the case in the lower Tertiary strata of the northern Great Plains in general and in western North Dakota specifically. This information exists as published and unpublished but accessible documents. The specific objective of this project is to implement, through computer-based data management systems, specific test area field studies that utilize all currently available information for the assessment of efficient database management techniques in the evaluation of specific coal correlation problems. This project is specific to fundamental coal resource and geologic studies undertaken by MMRRRI. There is no attempt to duplicate the general needs of a national database resource management program, which, by its very nature, must approach coal correlation at a more general level, dependent entirely on the nature of data inputted to it. The databases described above are multidisciplinary and aimed at resolving specific questions of a litho-, bio-, and chronostratigraphic correlation.

The focus of the first phase of this project was to establish the computerized basis for reevaluating North Dakota's lignite resource in a stratigraphic and paleontologic context. The goal of the second phase of the project was to establish more realistic database case studies, including surface and subsurface data specifically taken with the design and construction of stratigraphic and paleontologic databases as a resulting product. The third phase continues to set new and greater demands on the stratigraphic database design. Several thousand surface and subsurface data entries have been compiled from the uppermost Cretaceous and Paleocene Fort Union coal region of the Williston Basin, far-western North Dakota and adjacent easternmost Montana. Database designs have continued to be modified to reflect a greater knowledge on the demands and needs of the end-user. Unlike other databases that are constructed to summarize the data compiled, database research under the Coal Science program has attempted to design a flexible data management system that serves an ongoing interactive need to answer previously unconsidered resource-based questions.

Coal Science data management research will continue into the next biennium to conclude tasks concerning database programming. A number of new programming techniques have been developed that will significantly increase the relational power of existing databases, reducing the redundancy of forms for certain data retrieval operations. These database design improvements will be accomplished as an extension of the current cooperative agreement (as per the April 1992 monthly report) with existing funds.

4.0 REFERENCES

- LeFever, R.D., and Murphy, E.C., 1983, Mining resources and potential problems associated with mining of Cenozoic rocks of the Williston and Powder River Basins, northern Great Plains: North Dakota Mining and Mineral Resources Research Institute, Bulletin No. 83-09-MMRRRI-01, 170 p.
- Hartman, J.H., 1990a, Paleocene and Lower Eocene nonmarine molluscan biostratigraphy of the Powder River Basin, Wyoming-Montana: Geological Society of America, Rocky Mountain Section, Abstracts with Programs, v. 22, no. 6, p. 14.

- Hartman, J.H., 1990b, Coal science: Annual technical progress report for the period July 1, 1989, through June 30, 1990, including the quarterly technical progress report for the period April through June 1990, DE-FC21-86MC10637.
- Hartman, J.H., 1991a, Coal science: Earth resource evaluation and management: Semiannual technical report for the period January through June 1991, DE-FC21-86MC10637: Laramie, Wyoming.
- Hartman, J.H., 1991b, The stratigraphic distribution of nonmarine Mollusca across the Cretaceous-Tertiary boundary in the northern Great Plains, *in* the theme session "Nonmarine fossil record at the Cretaceous-Tertiary boundary": Geological Society of America, Abstracts with Programs, v. 23, no. 5, p. A359.
- Hartman, J.H., and Kihm, A.J., 1991, Stratigraphic distribution of *Titanoides* (Mammalia: Pantodonta) in the Fort Union Group (Paleocene) of North Dakota, *in* Christopher, J.E., and Haidl, F.M., eds., Sixth International Williston Basin Symposium: Saskatchewan Geological Society, Special Publication no. 11, p. 207-215.
- Hartman, J.H., 1992a, Coal science: Earth resource evaluation and management: Semiannual technical report for the period July through December 1991, DE-FC21-86MC10637: Laramie, Wyoming.
- Hartman, J.H., 1992b, Fossil as a resource in research, education, and economics in North Dakota: North Dakota Academy of Science, v. 46 (84th Annual Meeting), p. 2.
- Hartman, J.H., 1992c, Fossil invertebrates as a resource in research, education, and economics in North Dakota: North Dakota Academy of Science, v. 46 (84th Annual Meeting), p. 4.
- Hartman, J.H., 1992d, Biochronology of uppermost Cretaceous and lower Tertiary nonmarine mollusca of the northern Great Plains, U.S.A. and Canada, *in* the Fifth North American Paleontological Convention (Chicago), Abstracts with Programs: The Paleontological Society, Special Publication, No. 6, p. 123.
- Hartman, J.H., and Kihm, A.J., eds., 1992, A Symposium on the "Paleontology in North Dakota: Fossils as a resource in research, education, and economics": North Dakota Academy of Science, v. 46 (84th Annual Meeting), p. 1-10.
- Hartman, J.H., and Kihm, A.M., (in press, 1992), Chronostratigraphy of Paleocene strata in the Williston Basin, *in* Finkelman, R.B., Daly, D.J., Tewalt, S.J. (eds.), Geology and Utilization of Fort Union Region Lignites.
- Hartman, J.H., and Cvancara, A.M., (in preparation, 1992), Paleontology and biostratigraphy of the brackish and freshwater Mollusca of the Paleocene Slope (Ludlow) Formation of southwestern North Dakota and southeastern Montana, *in* Belt, E.S., and Daly, D.J., eds. [in preparation].

- Hartman, J.H., (for 1992 submission), Type and other historic molluscan localities from the Upper Cretaceous Fruitland and Kirtland Formations, San Juan Basin, New Mexico-Colorado: New Mexico Geological Society, Annual Field Guidebook.
- Hartman, J.H., (in preparation, 1993; by accepted abstract), Cretaceous and Paleocene stratigraphy and paleontology of eastern portion of the Crazy Mountains Basin, Montana: Road log and overview of recent investigations: Montana Geological Society, Energy and Mineral Resources of Central Montana, 1992 Field Conference Guidebook.
- Hartman, J.H., and Roth, B., (in preparation, 1993), Stratigraphy and paleontology of a diverse assemblage of nonmarine Mollusca from the Sentinel Butte Formation of North Dakota.
- Kihm, A.J., and Hartman, J.H., 1991, The age of the Sentinel Butte Formation, North Dakota: Society of Vertebrate Paleontology, Journal of Vertebrate Paleontology, v. 11, supplement to no. 3, p. 40a.
- Krause, D.W., Wunderlich, R., Hartman, J.H., and Kroeger, T.J., (in press, 1992), Latest Cretaceous and early Paleocene mammals from Makoshika State Park, Williston Basin, eastern Montana: Society of Vertebrate Paleontology (Toronto).
- Krause, D.W., Wunderlich, R., Hartman, J.H., Kroeger, T.J., and Peck, W.D., (in preparation, 1992), Latest Cretaceous and early Paleocene mammals from Makoshika State Park, Williston Basin, eastern Montana.

APPENDICES

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APPENDIX I

Document 1

*MNOS Database Form (Q&A® File Module)

Mno:	REF:	DATE:
P:	PAG:	LOG:
ent:	refBOSS:	from:
dFU:	secDONEon:	by:
UNQ:	intBY:	from:
OFno:	NAME:	Last Modified
REF#:	ADD#:	(Date) (Time)
INST:	#:	24K: 100K:
LOGt:	U: LOGcom:	NCRDS: SUMc: HEADc: LOGc:

NAT:	REG:	FIELD:	ldg:	I#:	O:
ST:	CO:	QD:	YR:	SR:	CI:
BLM:	QQ:	SEC:	T:	NS:	R:
TK/ft:	/m:	S/:	LG:	LT:	EW:
ELtop:	T/m:	X:	gd:	gm:	gs:
ELbot:	B/m:	Z:	Ng:	UTM:	Eg:
EL+/-:	+/-m:	CNS:	CO1:	CEW:	CO2:
INT:		ftNS:	#3:	ftEW:	#4:
		mNS:	#5:	mEW:	#6:

FS: Lno :
LS: RK-S:

SE4:	FM:	TK:	TKm:	4:	S:	F:
SE3:	FM:	TK:	TKm:	3:	S:	F:
SE2:	FM:	TK:	TKm:	2:	S:	F:
SE1:	FM:	TK:	TKm:	1:	S:	F:

PRIMARY FM:
ORG BED NAME: U#: U-TK/ft: U-TK/m:
REVISED NAME: BEDc: FD: XS: CL:

NAMED BEDS:

STRAT:

LOC:

COM:

PROPOwner:

PICTURES:

APPENDIX I

Document 2

*MNOS Database Form with Data (Q&A® File Module)

Mno: M2253 REF: Hartman (1990u, v. 18) DATE: 1990/09/05
P: PAG: p. 67, 106, 107-111, 112-115, 118-119, 124 LOG: 1990/10/02
ent: JHH refBOSS: Hartman, J.H. from: UND-EERC-MMRRI
dFU: secDONEon: 1990/09/08 by: Kroeger, T.J., Peck, W.D., Har
UNQ: M2253P intBY: Hartman, J.H. from: UND-EERC-MMRRI
OFno: No. 1-DH surface section NAME: M2187-DH surface sect Last Modified
REF#: M2253 ADD#: 1992/01/15 15:25 p.m.
INST: #: 24K: Y 100K: Y
LOGt: MS U: LOGcom: NCRDS: SUMc: HEADc: LOGc:

NAT: USA REG: WB-LMR FIELD: Brown Ranch ldg: 46103 I#: E7 0: m
ST: ND CO: Slope QD: Three V Crossing YR: 1979 SR: 7.5 CI: 20
BLM: QQ: about C E SE SEC: 9 T: 135 NS: N R: 105 EW: W SC: TC: RC:
TK/ft: 211.939 /m: 64.600 S/: LG: LT:
ELtop: 2857.743 T/m: 871.051 X: gd: gm: gs: td: tm: ts:
ELbot: 2645.785 B/m: 806.445 Z: Ng: UTM: Eg: UTM:
EL+/-: 10.0 +/-m: 3.0 CNS: CO1: CEW: CO2:
INT: JHH ftNS: #3: ftEW: #4:
mNS: #5: mEW: #6:
FS: B/? Lno : L5605 L5606 (Cannonball, upper tongue); L5607 (upper tongue?)
LS: RK-S:

: M2253 : Hartman (1990u, v. 18)

SE4: PAL FM: Slope TK: 106.626 TKm: 32.500 4: S: E1A F: T2
SE3: PAL FM: Cannonball-Upper? TK: 14.764 TKm: 4.500 3: S: E1A F: T2
SE2: PAL FM: Cannonball-Upper TK: 16.404 TKm: 5.000 2: C S: E1A F: T2
SE1: PAL FM: Slope TK: 80.708 TKm: 24.600 1: S: E1A F: T2

PRIMARY FM: Cannonball
ORG BED NAME: upper tongue U#: 029-031 U-TK/ft: 16.404 U-TK/m: 5.000
REVISED NAME: Three V Tongue BEDc: FD: XS: CL:

NAMED BEDS: Lower Coal Pair; Upper Coal Pair; Glasswort? clay; West Yellow
Marker; upper tongue; upper tongue?; No. 1 coal; Yule coal; ESB Channel 12

STRAT: This section plots on the location of M320 of Moore (1976).
Comparable sections include M40 and M51 by Belt. This section includes the
upper tongue (unpublished Three V Tongue) of the Cannonball Formation and a
number of coal beds.

: M2253 : Hartman (1990u, v. 18)

LOC: M2253, measured more or less due south of the drilling site M2187, is
located on generally south-facing exposures on a major bluff face and
associated tributary trending northwest to southeast. Section M2253a was
measured by Wes on the walls of the drilling mud pit.

COM: This surface section was measured to permit a direct comparison (by the
same geologists) with the upper portion of drill hole section M2187.

PROPOwner: U.S. Forest Service.

PICTURES: C1737-C1745, C1746-C1749 (localities), C1750-C1755

APPENDIX I

Document 3

*MNOS Database Form (Q&A® Write Module)

WILLISTON BASIN M-NUMBER LOCALITY FORM

Joseph H. Hartman, UND-EERC-MMRRI

data entered on: : form printed on: 1992/01/15

Example

LOG TYPE:

REFERENCE :
REFERENCE BOSS : ()
OBSERVATION BY : ()
INTERPRETED BY : ()
REFERENCE # :
ORIGINAL FIELD# :
INSTITUTION # :
DRILL LOG TYPES :
FOSSIL L-numbers : ()

ADDITIONAL # :
LOCALITY NAME :
PANEL DATA : AREA CROSS SEC COLUMN
NCRDS RELATED : NCRDS: SUMc: HEADc: LOGc:

M-number LOCATION DATA

GENERAL LOCATION : , , County STUDY AREA: region, field area
QUADRANGLE DATA : Quad., , series, foot contour interval (map location: ,)
LEGAL LOCATION : sec., T., R., (CODES- sec: ; TWP: ; RGE: ; X: ; BLM:)
FROM SECTION LINE : feet, feet; meters, meters
ILLUSTRATIONS : PLOTTED (Y/N)- 24k: 100k:
SITE DESCRIPTION :

STRATIGRAPHIC DATA

Litho- and Chronostratigraphy of Section (1 to 4 = bottom to top)

SERIES4:	FORMATION:	THICKNESS:	feet;	meters	C4:
SERIES3:	FORMATION:	THICKNESS:	feet;	meters	C3:
SERIES2:	FORMATION:	THICKNESS:	feet;	meters	C2:
SERIES1:	FORMATION:	THICKNESS:	feet;	meters	C1:

Section Thickness and Elevations

SECTION THICKNESS : feet; meters
ELEV TOP OF SECTION : feet; meters ELEVATION +/- : feet; meters
ELEV BASE OF SECTION : feet; meters INTERPRETED BY :

Bed Nomenclature and Data

PRIMARY FORMATION :
ORIGINAL BED NAME :
REVISED BED NAME :
NAMED BEDS IN SECTION :
LITHIC COLLNS :
UNIT # : BED Code:

Stratigraphic Correlation and Description

GENERAL M-number COMMENTS

APPENDIX I

Document 4

*MNOS Database Example (Q&A® Write Module)

WILLISTON BASIN M-NUMBER LOCALITY FORM

Joseph H. Hartman, UND-EERC-MMRRI

data entered on: 1990/10/02; form printed on: 1992/01/15

M2253

LOG TYPE: MS

REFERENCE : Hartman (1990u, v. 18), p. 67, 106, 107-111, 112-115, 118-119, 124-128, 148-150, 155-157
REFERENCE BOSS : Hartman, J.H. (UND-EERC-MMRRI)
OBSERVATION BY : Kroeger, T.J., Peck, W.D., Hartman, J.H. (1990/09/08)
INTERPRETED BY : Hartman, J.H. (UND-EERC-MMRRI)
REFERENCE # : M2253 ADDITIONAL # :
ORIGINAL FIELD# : No. 1-DH surface section LOCALITY NAME : M2187-DH surface section
INSTITUTION # : PANEL DATA : AREA CROSS SEC COLUMN
DRILL LOG TYPES : NCRDS RELATED : NCRDS: SUMc: HEADc: LOGc:
FOSSIL L-numbers : L5605-L5606 (Cannonball, upper tongue); L5607 (upper tongue?) (B/?)

M-number LOCATION DATA

GENERAL LOCATION : USA, ND, Slope County STUDY AREA: WB-LMR region, Brown Ranch field area
QUADRANGLE DATA : Three V Crossing Quad., 1979, 7.5 series, 20 foot contour interval (map location: 46103, E7)
LEGAL LOCATION : about C E SE sec. 9, T. 135 N., R. 105 W. (CODES- sec: ; TWP: ; RGE: ; X: ; BLM:)
FROM SECTION LINE : feet , feet ; meters , meters
ILLUSTRATIONS : C1737-C1745, C1746-C1749 (localitie PLOTTED (Y/N)- 24k: Y 100k: Y
SITE DESCRIPTION : M2253, measured more or less due south of the drilling site M2187, is located on generally south-facing exposures on a major bluff face and associated tributary trending northwest to southeast. Section M2253a was measured by Wes on the walls of the drilling mud pit.

STRATIGRAPHIC DATA

Litho- and Chronostratigraphy of Section (1 to 4 = bottom to top)

SERIES4: PAL	FORMATION: Slope	THICKNESS: 106.626 feet; 32.500 meters	C4:
SERIES3: PAL	FORMATION: Cannonball-Upper?	THICKNESS: 14.764 feet; 4.500 meters	C3:
SERIES2: PAL	FORMATION: Cannonball-Upper	THICKNESS: 16.404 feet; 5.000 meters	C2: C
SERIES1: PAL	FORMATION: Slope	THICKNESS: 80.708 feet; 24.600 meters	C1:

Section Thickness and Elevations

SECTION THICKNESS : 211.939 feet; 64.600 meters
ELEV TOP OF SECTION : 2857.743 feet; 871.051 meters ELEVATION +/- : 10.0 feet; 3.0 meters
ELEV BASE OF SECTION : 2645.785 feet; 806.445 meters INTERPRETED BY : JHH

Bed Nomenclature and Data

PRIMARY FORMATION : Cannonball LITHIC COLLNS :
ORIGINAL BED NAME : upper tongue UNIT # : 029-031 BED Code:
REVISED BED NAME : Three V Tongue
NAMED BEDS IN SECTION : Lower Coal Pair; Upper Coal Pair; Glasswort? clay; West Yellow Marker; upper tongue; upper tongue?; No. 1 coal; Yule coal; ESB Channel 12

Stratigraphic Correlation and Description

This section plots on the location of M320 of Moore (1976). Comparable sections include M40 and M51 by Belt. This section includes the upper tongue (unpublished Three V Tongue) of the Cannonball Formation and a number of coal beds.

GENERAL M-number COMMENTS

This surface section was measured to permit a direct comparison (by the same geologists) with the upper portion of drill hole section M2187.

APPENDIX I

Document 5

***MNOS Database Fields Organized by Topic (Q&A® File Module)**

See Document 6 for full Field Names and Explanations

REFERENCE RELATED INFORMATION

Numbering Systems Fields

Mno:
OFno:
REF#:
ADD#:
INST: #:

Reference (Citation) Fields

REF:
PAG:
refBOSS: from:
secDONEon: by:
intBY: from:
NAME:
LOGt: LOGcom:
FD: XS: CL:
COM:
PICTURES:

Record Management Fields

DATE: (of Reference)
LOG: (of entry)
P:
UNQ:
ent:
LAST MODIFIED Fields – Date and Time of modification
24K: 100K:
U: (utility)
NCRDS: SUMc: HEADc: LOGc:
O: (original unit of measure)

Screen Management Fields

[Mno]: [REF]: (for screens 2 and 3)

LOCATION FIELDS

General Location

NAT: ST: CO:
REG: FIELD:
QD: YR: SR: CI: ldg: I#:
LOC:
PROPowner:

***MNOS Database FIELDS ORGANIZED BY TOPIC, continued**

LOCATION FIELDS, continued

Legal Location

BLM:
QQ: SEC: SC: T: NS: TC: R: EW: RC:
ftNS: #3: ftEW: #4:
mNS: #5: mEW: #6:
S/:
X:

Longitude and Latitude Coordinates

LG: LT:
gd: gm: gs: td: tm: ts:
X:

UTM Coordinates

Z: Ng: UTM: Eg: UTM:
X:

State Land Grid Coordinate System

CNS: C01: CEW: C02:
X:

STRATIGRAPHY FIELDS

Section Elevations

TK/ft: /m:
ELtop: T/m:
ELbot: B/m:
EL+/-: +/-m: INT:

Chronostratigraphy

SE4: S:
SE3: S:
SE2: S:
SE1: S:

Lithostratigraphy and Formation Thickness

FM: F: 4: TK: TKm:
FM: F: 3: TK: TKm:
FM: F: 2: TK: TKm:
FM: F: 1: TK: TKm:
PRIMARY FM:
NAMED BEDS:
STRAT:
dFU:

***MNOS Database FIELDS ORGANIZED BY TOPIC, continued**

STRATIGRAPHY FIELDS, continued

Unit (Bed) Nomenclature and Basic Data

ORG BED NAME:

REVISED NAME:

U#:

U-TK/ft: U-TK/m:

BEDc:

dFU:

SAMPLE COLLECTION FIELDS

Fossil Collections

FS: Lno:

Rock Collections

LS: RK-S:

APPENDIX I

Document 6

***MNOS Database Field Names and Explanations**

The following list contains the explanations of the typically abbreviated field names used in *MNOS databases in the File Module of Q&A®. The unabbreviated form of the field name is given parenthetically, followed by an explanation and/or examples of entry input to show the appropriate type of field information and style. This explanatory information is available to the Q&A® user through customized HELP fields while inputting or editing data. The fields are ordered as per row in *MNOS databases (see Appendix Document 4.2.1 for example).

Mno (M-number)

EERC MMRRRI section or geological observation number (e.g., M1000, M2345a). If this M-number entry (of the first screen or page) is inadvertently changed, the M-number entry of the second screen is not affected.

REF (Reference)

Primary reference information; examples of preferred formats: Hares (1928), Hartman (1986u), Hartman (1991u, v. 12) [u = unpublished]; U.S. Geological Survey OFR (for Open-file Reports); North Dakota Geological Survey; North Dakota State Water Commission. The primary reference information for this form is automatically entered on the second and subsequent pages (screens) in the ADD and UPDATE modes.

DATE (Date of Reference)

The date of the reference (REF) (e.g., 1978). Enter also the month and day if the reference is unpublished and the information is available (e.g., 1978/10/12).

P (Primary form)

Enter "P" for all primary forms. Leave empty for all other (duplicate = other use) forms.

PAG (Pagination)

Secondary reference information. For typical references, enter pagination, such as page (p.), plate (pl.), etc. The letters "m" and "p" adjacent to page numbers stand for "map" and "photo" (the pagination "p. 34p, 35, 36m" indicates that a photo and map of the section is found on pages 34 and 36, respectively). For drill holes use this line for source of information, such as "NCRDS summary form," "drilling form," etc.

LOG

Represents data of first or subsequent revisions of M-number data on computer. The date is automatically entered in the ADD mode when entering data to a new form. Major revisions to a previous form should receive a new date. Save an old form as a hard copy or as secondary forms (non-"P" forms).

ent (Enterer)

Enter the initials of person who is responsible for filling in form. Note the source of interpretations (location information, etc.) in fields **INT**, **STRAT**, **LOC**, or **COM**.

refBOSS (Reference boss)

Enter the last name and initials of the person in charge of the reference (e.g., Hares, C.J.). This entry may be the same as given under **REF**.

from

Enter the institutional affiliation of the **refBOSS** (e.g., University of North Dakota, U.S. Geological Survey, North Dakota Geological Survey).

dFU (Duplicate form)

This form is used to integrate the presence of partially "duplicate" forms in the database for use with data specific to formations and units. Enter "F" or "U" for use of same M-number for descriptions of formation or unit thicknesses within this section (this approach avoids duplication of an M-number in sort routines in general reference to location or other information about the section).

secDONEon (Date section was done)

Enter the date section was measured or drilled (e.g., month/day/year).

by

Enter the name of the person who measured the section (e.g., Powell, L.M.).

UNQ (Unique M-number)

This field is automatically entered combining fields **Mno** and **P** to make **LnoP** (e.g., M2187P). The purpose of this addition is to create a unique M-number for a variety of external lookup files.

intBY (Interpreted by)

Enter the person responsible for interpreting the section as given in this form. This may be the same person as given in fields **REF** (reference source) and **by** (section measurer). This use of this field is meant particularly for the subsequent interpretation of subsurface geophysical logs.

from

Enter the institutional affiliation of the **intBY** (e.g., University of North Dakota, U.S. Geological Survey, North Dakota Geological Survey).

OFno (Original field number)

Enter the number originally applied to the section. This number usually is the number (or name) assigned to the section during field work.

NAME (Name of section)

Enter the name of the section (e.g., Red Hills).

REF# (Reference number)

Enter the number applied to section in REF. This may or may not be the original field number (OFno). Both the original field number (OFno) and the reference number (REF#) should be entered even if they are the same.

ADD# (Additional number)

Enter any additional numbers that may have been used by REF to refer to this section. This field may also have a "constructed" number to use to help refer to a section that cannot otherwise be conveniently differentiated from another section.

Last Modified See DATE and TIME of last modification.

(DATE of Last Modification)

If ANY changes are made to this form, the date that those changes were made will automatically be entered in this field. The DATE field is otherwise invisible.

(TIME of Last Modification)

If ANY changes are made to this form, the time that those changes were made will automatically be entered in this field. The TIME field is otherwise invisible.

INST (Institution)

Enter the institutional acronym for use with a formalized numbering system (e.g., USGS, NDGS, NDSWC), and enter number in next field (#).

(Institutional number)

The identification number used in a formalized numbering system.

24K

Enter "P" if the locality has been plotted on 1:24,000-scale map.

100K

Enter "P" if the locality has been plotted on 1:100,000-scale map.

LOGt (Type of section)

Enter one of the following two-letter log codes: MS = measured section; DH = drill hole section; RR = rock record (single bed or rock sample occurrence); PM = paleomagnetic reading. A paleomagnetic section is a measured section if encompassing more than a single bed.

U (Unit type)

Enter one of the following user-specified unit type codes for reference to a bed or bed complex: BT = bed thickness (unspecified bed type); CB = Cannonball Formation (tongue); CS = coal section (coal thickness); PM = paleomagnetic (detail); QU = quarry section (fossil deposit) (limited use); SI = silcrete; WM = white marker.

LOGcom (Log comment)

Enter the appropriate geophysical log codes (e.g., 07, 08, 10, 11): 01 (core), 02 (drill hole), 03 (rotary), 05 (electric), 06 (geophysical), 07 (gamma), 08 (density), 09 (neutron), 10 (resistivity), 11 (spontaneous potential), 12 (sonic), 13 (laterlog), 14 (seismic), 15 (caliper), 16 (coal test), 17 (oil and gas), 18 (water well).

NCRDS (National Coal Resources Data System)

Enter "Y" (yes) to indicate that this M-number is to be used in the NCRDS program.

SUMc (NCRDS summary form copied)

Enter "C" (copied) to indicate if the associated NCRDS summary sheet(s) has(have) been copied and filed (this use is in reference to geophysical logs). Enter "P" to indicate that a photocopy has been made of a nongeophysical log record (this use is in reference to surface sections).

HEADc (Original header copied)

Enter "C" (copied) to indicate that the original header from the geophysical log has been copied and filed.

LOGc (Geophysical or other log copied)

Enter "C" (copied) to indicate that the entire geophysical log has been copied and filed.

NAT (Nation)

Enter a three-letter abbreviation for the nation of the locality (e.g., USA, CAN).

REG (Region)

Enter a regional designation for the locality. These designations are predetermined; examples for the Williston Basin are as follows: WB-NDC = central North Dakota; WB-LMR = Little Missouri River; WB-FTU = Fort Union; WB-W = Garfield and McCone Counties; WB-N = northern Montana; WB-SK = Saskatchewan.

FIELD (Field or study area)

Enter the name of the field or study area (if available) in which the locality occurs (e.g., Williston lignite field, Charlson oil field). The field area is an area smaller than a region (REG) and generally is an area designated by the reference (REF).

1dg (1 degree)

Enter the 1 x 1-degree reference number cited by USGS in state quadrangle booklets (automatically entered after leaving field QD).

I# (Map Index number)

Indexes quadrangles within 1 x 1-degree areas by the USGS methods. This field is automatically filled upon leaving the QD field.

O (Original units of measure)

Enter "ft" or "m" to indicate in what units the original section was measured.

ST (State or Canadian Province)

Enter the two-letter designation for the state or province as per U.S. Postal standards.

CO (County)

Enter the name of the county in which the section occurs.

QD (Quadrangle)

Enter the name of USGS 7.5-minute quadrangle on which the section is located.

YR (Year quadrangle was published)

This field is automatically filled upon leaving the field QD.

SR (Map series)

The appropriate U.S. Geological Survey map series (e.g., 7.5, 15) (7.5-minute = 1:24,000; 15-minute = 1:62,500 (not typically used) will be automatically entered upon leaving the QD field.

CI (Contour interval)

The contour interval for all 7.5-minute maps is presently in feet. This field is automatically entered upon leaving the QD field (if the data has been inputted in the MAPS database).

BLM (Bureau of Land Management [and others])

Enter, if used in the original reference, the section subdivision system with letters to refer to quarter section areas (cartesian quadrants) (e.g., ADC). Entered subdivisions will automatically be converted to quarter-quarter (QQ) nomenclature (e.g., SW SE NE).

QQ (Quarter section subdivisions)

Enter the quarter section subdivision (e.g., SW SE NW) for the location of the locality. Use other descriptive terms as necessary, e.g., C west edge (C = center); near; about; central.

SEC (Section)

Enter the section number in which the M-number occurs. If the M-number occurs in more than one section (as with a measured section), place the appropriate code in the field SC.

T (Township)

Enter the township number in which the section occurs (e.g., 124). Enter the number only. Do not enter the preceding "T" or the subsequent "N" or "S."

NS (North/South)

Enter N or S in reference to townships north or south of the base line.

R (Range)

Enter the range number in which the locality occurs (e.g., 84). Enter the number only. Do not enter the preceding "R" or the subsequent "E" or "W."

EW (East/West)

Enter E or W in reference to townships east or west of the principal meridian.

SC (Section code)

Enter "?" if there is uncertainty in the section designation (used primarily for historical records with inspecific data). Enter "/" if a locality occurs in more than one section, and enter this additional section in the field S/.

TC (Township code)

Enter "?" if there is uncertainty in the township designation (used primarily for historical records with inspecific data). Enter 2pm (2nd principal meridian), 3pm (3rd principal meridian), etc., for reference to Canadian principal meridians.

RC (Range code)

Enter "?" if there is uncertainty in the range designation (used primarily for historical records with inspecific data).

TK/ft (Section thickness in feet)

Enter the thickness of the section in feet. If section thickness was originally measured in meters, this field will be inputted automatically upon leaving the field TK/m.

TK/m (Section thickness in meters)

Enter the thickness of the section in meters. If section thickness was originally measured in feet, this field will be inputted automatically upon leaving the field TK/ft.

S/ (Additional township and range section number)

Enter the additional section number (e.g., 24) in which the locality occurs. This section is in reference to the section number given in field SEC.

LG (Longitude)

Enter longitude of the locality in the following format: ###.####.

LT (Latitude)

Enter the latitude of the locality in the following format: ##.####.

ELtop (Elevation at top of section or unit in feet)

Enter elevation (in feet) at the top of the geologic section or unit. If the elevation was originally entered in meters, leave this field blank. The conversion from meters to feet will be done automatically.

T/m (Elevation at top of section in meters)

Enter, in meters, the elevation of the top of the section (if interpreted originally in meters). The elevation in feet will be automatically entered in field ELtop upon leaving T/m.

X (Coordinate location code)

Enter "X" to indicate that the coordinate system location was based on an arbitrarily plotted point (where the locality was only known to an area).

gd (Longitude value for degrees)

This value is automatically extracted from the longitude value.

gm (Longitude value for minutes)

This value is automatically extracted from the longitude value.

gs (Longitude value for seconds)

This value is automatically extracted from the longitude value.

td (Latitude value for degrees)

This value is automatically extracted from the latitude value.

tm (Latitude value for minutes)

This value is automatically extracted from the latitude value.

ts (Latitude value for seconds)

This value is automatically extracted from the latitude value.

ELbot (Elevation at bottom of section in feet)

Enter elevation (in feet) at the bottom of the geologic section. If the elevation was originally entered in meters, leave this field blank. The conversion from meters to feet will be done automatically.

B/m (Elevation of bottom of section in meters)

Enter, in meters, the elevation of the base of the section (if interpreted originally in meters). The elevation in feet will be automatically entered in field ELbot upon leaving B/m.

Z (Zone of UTM coordinate system)

Enter the zone number (e.g., 12) for the following UTM coordinate.

Ng (Northing for UTM coordinate system)

This value is preset for northing (N).

UTM (Universal Transverse Mercator coordinate system easting number)

Enter the easting number; commas are automatically emplaced.

Eg (Easting for UTM coordinate system)

This value is preset for easting (E).

UTM (Universal Transverse Mercator coordinate system northing number)

Enter the northing number; commas are automatically emplaced.

EL+/- (Elevation accuracy in feet)

Enter the letters "A" (= approximate) or "vA" (= very approximate) as estimates of the locality's elevation, or enter the footage value based on an interpretation of contours on a topographic map (e.g., "10" = +/- 10 ft).

+/-m (Elevation accuracy in meters)

Enter the letters "A" (= approximate) or "vA" (= very approximate) as estimates of the locality's elevation, or enter the metric value based on an interpretation of contours on a topographic map (e.g., "3" = +/- 3 m). As most elevation contour lines on U.S. Geological Survey topographic maps are in feet, a numeric value given in field "EL+/-" will automatically be converted to meters in this field (" +/-m).

INT (Interpreter of elevation)

Enter the initials of person making the interpretation of the elevation.

CNS (North/south code)

As appropriate, enter "N" (north) or "S" (south) zone code for the 10,000-ft state plane coordinate system.

C01 (10,000 ft coordinate number)

Enter the 10,000-ft coordinate number appropriate for the location of the locality. This number is read from a USGS quadrangle (commas are applied to this number automatically).

CEW (East/west code)

As appropriate, enter "E" (east) or "W" (west) zone code for the 10,000-ft state plane coordinate system.

C02 (10,000 ft coordinate number)

Enter the 10,000-ft coordinate number appropriate for the location of the locality. This number is read from a USGS quadrangle (commas are applied to this number automatically).

ftNS (Feet north or south of section line)

Enter "N" or "S" to indicate in which direction the distance from a section line was measured. This field is automatically filled if the metric value is entered in Field #5.

#3 (Number of feet north or south of a section line)

Enter the distance in feet north or south of a section line.

ftEW (Feet east or west of a section line)

Enter "E" or "W" to indicate in which direction the distance from a section line was measured. This field is automatically filled if the metric value is entered in Field #6.

#4 (Number of feet east or west of a section line)

Enter the distance in feet east or west of a section line.

mNS (Meters north or south of a section line)

Enter "N" or "S" to indicate in which direction the distance from a section line is measured. This field is filled automatically if ftNS is entered.

#5 (Number of meters north or south of a section line)

Enter the distance in meters north or south of a section line. This field is automatically filled if #3 is entered.

mEW (Meters east or west of a section line)

Enter "E" or "W" to indicate in which direction the distance from a section line is measured. This field is filled automatically if ftEW is entered.

#6 (Number of meters east or west of a section line)

Enter the distance in meters east or west of a section line. This field is automatically filled if #4 is entered.

FS (Fossil samples)

Enter "Y" (yes) if fossils have been collected from this section (locality numbers are entered in field Lno). Enter "x" (= yes) if fossils were collected but no L-number has yet been assigned.

Lno (L-number)

Enter L-numbers assigned to this section. The L-number represents a paleontological locality numbering system initiated and maintained by Joseph H. Hartman.

LS (Lithic cutting or samples)

Enter "Y" (yes) if sample has been numbered and then see field RK-S.

RK-S (Lithic sample number)

Enter rock sample numbers assigned to this section.

SE4 (Epoch)

Enter the series abbreviation applicable to formation #4 (FM4) (e.g., EOC = Eocene; PAL = Paleocene; UK = Upper Cretaceous).

FM (Formation)

Enter a formation name occurring in the section. Formations are ordered as per their stratigraphic superposition (see SERIES1-SERIES4), with SERIES1 (or Formation 1) as the oldest and SERIES4 as the most recent.

TK (Formation thickness in feet)

Enter the thickness, in feet, of Formations 1-4, respectively. If the original measurement was in meters, a conversion to feet is automatically done upon leaving the appropriate TKm field.

TKm (Formation thickness in meters)

Enter the thickness, in meters, of Formations 1-4, respectively, if the section was originally measured in meters. The calculation to meters from feet is done automatically after the footage is entered in field TK. If the original measurement was in meters, a conversion to feet is automatically done upon leaving the appropriate TKm field.

4 (Formation code)

Enter the formation code ("C") for Formations 1-4, respectively, if the formation is complete in this section.

S (Series code)

The series code for Formations 1-4 (FM), respectively, is automatically entered upon leaving the SE(1-4) fields.

F (Formation code)

The formation code for Formations 1-4 (FM), respectively, is entered automatically upon leaving the FM fields.

PRIMARY FM (Primary Formation)

Enter the name of the primary formation in the section.

ORG BED NAME (Original bed name)

Enter the original name of the bed or unit (if the purpose of the form is to consider individual units).

U# (Unit number)

Enter the unit number of a specific bed in the section. Refer to the *UNITS file for more complete information on this unit.

U-TK/ft (Unit thickness)

Enter the thickness, in feet, of the unit referred to in field U#.

U-TK/m (Unit thickness)

Enter the thickness, in meters, of the unit referred to in field U#.
This value is automatically derived from the field U-TK/ft if the value was originally measured in feet.

REVISED NAME (Revised bed name)

Enter the revised name of the bed referred to in **ORG BED NAME**. Include the initials of the person making the revision along with the year (if necessary) and the lithology (e.g., lignite Bed B-FAH 1928).

BEDc (Bed code)

Enter one of the following bed codes: ? = questioned correlation; + = bed thicker than given (bed not totally exposed); T = possible stratotype (TYPE) for bed; C = clinker bed representing the product of a burned named bed; P = parting > or = to 10% or < 25% of bed thickness (otherwise no "P"); S = split - parting > or = 25% of bed thickness.

FD (Project number)

The project field represents a subdivision of the field **REG**, as used in Hartman (1984) for the location of cross section panels and corresponds to the "zone" field area.

XS (Cross section or panel identifier)

Enter the number of the cross section in which the geologic section has been illustrated.

CL (Column number)

Enter the number of the column in the cross section (XS) that refers to a particular M-number geologic section.

NAMED BEDS

Enter the names (formal or informal) of beds occurring in this section.

STRAT (Stratigraphy)

Enter, preferably as a quote, any general stratigraphic comments.

LOC (Location)

Enter, preferably as a quote, any general location comments.

COM (Comments)

Enter any general comments about the section that do not fit well into any other field.

PROPOwner (Property owner)

Enter the name of the owner of the property on which the section is located.

PICTURES

Enter the catalog number of photographs of the section or unit (taken in the field or lab).

APPENDIX II

Document 7

*UNIT Database Form (Q&A® File Module)

Mno:	REF:	DATE:	
SC:	PAG:	LOG:	
ST: REG:	PJC:	mod: (Date) (Time)	ent:

U#:	M#+U#:	O:	BED:
DV:	x:	SCALE:	FM:
+	COM:		
TK/ft:	SC-EL/Top:	SC-TK/ft:	Lnos:
TK/m :	SC-EL/Bot:	SC-TK/m :	RK-S:

DESC:

End of first
screen

STRATCOL-LITH :	SYMBOL:	RESISTANCE VALUE:
LITHOLOGY:	modifier:	
COLOR:	FRESH/DRY:	GSAcOLOR: NUM:
COLOR(COM):		
SEQU :	S/S :	

M#: REF:

F-ENVIR:
S-ENVIR: COM2:

<p style="text-align: center; margin: 0;">SECTION STRUCTURAL INFORMATION</p> <p>fct:</p> <p>DIP: DIPrad:</p> <p>PACE: fctval:</p> <p>SURF: U-TK:</p> <p>SURF-T: SC-TK:</p>	<p style="text-align: center; margin: 0;">NCRDS DATA FIELDS UQ:</p> <p>prILITH: modLITH:</p> <p>COLOR:</p> <p>GRsize: GRshape:</p> <p>MINERALS:</p> <p>BEDDING: CONTACT:</p> <p>FOSSILS:</p> <p>FRACTURES: JOINTS:</p> <p>CLEATS:</p> <p>WILD1: WILD2:</p> <p>COMMENT:</p>
--	--

<p style="text-align: center; margin: 0;">STRATIFACT/LOGGER FIELDS</p> <p>M#-U#:</p> <p>U-top: U-top-EL:</p> <p>U-bot: U-bot-EL:</p>
--

APPENDIX II

Document 8

*UNIT Database Form with Data (Q&A® File Module)

Mno: M2253 REF: Hartman (1990u, v. 18) DATE: 1990/09/09
SC: MS PAG: p. 148-150 (see v. III, p. 33-41, 48-61) LOG: 1990/09/12
ST: ND REG: WB-LMR PJC: Slope mod: 1992/01/15 15:25 p.m. ent: JHH

U#: 043	M#+U#: M2253-043	O: m	BED: Yule coal-JHH
DV:	x:	SCALE:	FM: Slope
+	COM:		
TK/ft: 3.937	SC-EL/Top: 2857.724	SC-TK/ft: 211.939	Lnos:
TK/m : 1.200	SC-EL/Bot: 2645.785	SC-TK/m : 64.600	RK-S:

DESC: "lignite, black (N 1)"

STRATCOL-LITH : lig	SYMBOL: LIG	RESISTANCE VALUE: 1
LITHOLOGY: lignite	modifier:	
COLOR: black	FRESH/DRY: F	GSAcOLOR: N 1
COLOR(COM):		NUM: 11.50
SEQU :	S/S :	

M#: M2253 REF: Hartman (1990u, v. 18)

F-ENVIR:

S-ENVIR: coal swamp

COM2:

SECTION STRUCTURAL INFORMATION	NCRDS DATA FIELDS UQ:
fct:	priLITH: modLITH:
DIP:	COLOR:
PACE:	GRsize: GRshape:
SURF:	MINERALS:
SURF-T:	BEDDING: CONTACT:
	FOSSILS:
	FRACTURES: JOINTS:
	CLEATS:
	WILD1: WILD2:
	COMMENT:

STRATIFACT/LOGGER FIELDS	
M#-U#:	
U-top:	U-top-EL:
U-bot:	U-bot-EL:

APPENDIX II
Document 9
*UNIT Database Report (Q&A® Report Module)

Units Summed from Base with Elevations & Descriptions: M2253
(Hartman, 1990u, M2187-DH surface section)

MMRRI Sect.	Unit	Feet	Elevation			
Sect. No.	Unit No.	THICK ft	Above Base of Section	ABV Base of Section	Bed Name	Fossil LOC #
M2253	057	0.000	211.939	2857.763		Top of section.
	056	8.202	211.939	2857.724	Slope	"covered interval of siltstones and claystones to highest ground on plateau (west of well)" See M2253a for mud pit section through this interval.
	055	2.953	203.737	2849.522	Slope	"deeply weathered silty claystone, bentonitic; ironstone concretion on surface; dusky yellowish brown (10 YR 2/2)"
	054	10.663	200.784	2846.569	ESB Channel 12-JHH Slope	"siltstone to very fine-grained sandstone; includes concretion horizon near top (better lithified lens); small ripples; root traces; pale yellowish orange (10 YR 8/2)"
	053	4.921	190.121	2835.906	Slope	"silty claystone, somewhat fissile; plant fragments; discontinuous concretionary zone at top; dark yellowish brown (10 YR 4/2)"
	052	0.984	185.200	2830.985	unnamed lignite-JHH	"lignite, black (N 1)"
	051	0.656	184.216	2830.001	Slope	plants "Carbonaceous shale; extensively rooted; abundant plant fragments; dusky yellowish brown (10 YR 2/2)"
	050	9.186	183.560	2829.345	Slope	"light olive gray (5 Y 6/1) clayey siltstone in lower part coarsening upwards in middle with 3 or 4 thin (5 cm) beds of fine-grained sandstone, fining upwards in upper part to silty claystone; dark yellowish brown (10 YR 4/2); 20 cm thick concretionary bed 1 m above base " Uppermost horizon of bentonitic slope wash.
	049	2.625	174.374	2820.159	Slope	"organic rich silty claystone; bentonitic, crumbly; upper and lower contacts are gradational; slickensides; root traces; pale yellowish brown (10 YR 6/2) to dark yellowish brown (10 YR 4/2)" Photos lateral to bentonitic slope wash, including units 45 to near top.
	048	0.984	171.749	2817.534	Slope	"carbonaceous shale, slightly lignitic; brownish black to grayish black (5 YR 2/1 to N 2); lignite clasts are black (N 1)" Slope is covered by popcorn clay.
	047	2.297	170.765	2816.550	Slope	"silty claystone to claystone (fining upwards), silty at base; extensively rooted; slickensides; organic laminae at bottom; large horizon roots (rhizomes);

APPENDIX II
Document 10
NCRDS *UNIT Database Form with Data (Q&A® Write Module)

USGS NATIONAL COAL RESOURCES DATA SYSTEM - STRATIGRAPHIC DATA FORM - USTRAT
printed: 1992/01/15

POINT ID: M2688		GEOLOGIST: Schmit, C.R.		DATE: 1977	CONFID:
QUAD+SER: Scranton NE	7.5	SOURCE: NCRDS summary form		PRIN MERIDIAN: 07	
STATE: ND		SURF-ELEV: 2809.000	EST-RANK: lignite	QUARTERS: NW NW SE	
COUNTY: Bowman		ELVPREC:	STR-DIP:	SECTION: 21	
PROVINCE: N Great Plains		THICKNESS: 236.000	LATITUDE: 46 14	TOWNSHIP: 132 N	
REGION: Fort Union		DESCR-LOG:	LONGITUDE: 103 4	RANGE: 99 W	
FIELD:		WEATHERING:	LLPREC:		
COMMENT1: B077-105					
HYDRO CD:		FILEPOINTER:	OWNERSHIP:		

UNIT DATA

Explanation:

U# = Unit	prLITH = Primary lithology	grSHAPE = Grain shape	C = Fractures	WC1 = Wild card 1
UQ = Unit qualifier	modLITH = Lithology modifier	A = Contact	D = Joints	WC2 = Wild card 2
TK/Ft = Thickness (ft)	grSIZE = Grain size	B = Fossils	E = Cleats	

U#	UQ	TK/FT	Formation	Name	prLITH	modLITH	Color	grSIZE	grSHAPE	Minerals	Bedding	A	B	C	D	E	WC1	WC2	Comment2
001		20.500			NR														
002		0.500			NR	CARB													
003		1.500			NR														
004		0.500			NR	CARB													
005		13.500			NR														
006		1.500			NR	CARB													
007		39.000			NR														
008		2.000			NR	CARB													
009		4.000			NR														
010		3.000			NR	CARB													
011		1.000			NR														
012		2.500			NR	CARB													
013		1.000			NR														
014		2.000			NR	CARB													
015		10.000			NR														
016		1.000			NR	CARB													
017		2.500			NR														
018		3.500			LIG														
019		35.500			NR														
020		2.000			NR	CARB													
021		24.500			NR														
022		8.500			LIG														
023		7.000			NR														
024		0.500			NR	CARB													
025		1.000			NR														
026		4.000			LIG														
027		6.500			NR														
028		2.000			NR	CARB													
029		7.500			NR														
030		2.500			NR	CARB													
031		25.000			NR														

APPENDIX II

Document 11

***UNIT Database Fields Organized by Topic (Q&A® File Module)**

See Document 12 for full Field Names and Explanations

REFERENCE RELATED INFORMATION

Numbering Systems Fields

Mno:

U#:

Reference (Citation) Fields

REF:

PAG:

SC:

Record Management Fields

DATE:

LOG:

PJC:

mod:

ent:

M#+U#:

O:

Screen Management Fields

[Mno]: [REF]: (for screen 2)

LOCATION FIELDS

General Location

ST:

REG:

STRATIGRAPHY

Unit Thickness Calculations

DV: x: SCALE:

+:
TK/ft: TK/m:

SC-TK/ft: SC-TK/m:

SC-EL/Top: SC-EL/Bot:

Unit (Bed) Nomenclature and Basic Data

BED: Bed name (plus who assigned name)

FM: Formation (plus who assigned name)

COM: Comment

DESC: Unit description

***UNITS Database FIELDS ORGANIZED BY TOPIC, continued**

STRATIGRAPHY, continued

Unit (Bed) Data Categorization

LITHOLOGY: modifier:
COLOR: FRESH/DRY: GSAcolor: NUM: COLOR(COM):
SEQU: S/S:
F-ENVIR: S-ENVIR: COM2:

STRATCOL/STRATA Fields

STRATCOL-LITH: SYMPOL: RESISTANCE VALUE:

Section Structural Information Fields

fct: fctval:
DIP: DIPrad:
PACE:
SURF: SURF-T:
U-TK: SC-TK:

SAMPLE COLLECTION FIELDS

Fossil and Rock Collections

Lnos: RK-S:

NCRDS-SPECIFIC FIELDS

UQ: Unit Qualifier
priLITH: modLITH: primary lithology and lithic modifier
COLOR:
GRsize: GRshape: grain size and shape
MINERALS: BEDDING: CONTACT:
FOSSILS:
FRACTURES: JOINTS: CLEATS:
WILD1: WILD2:
COMMENT:

STRATIFACT/LOGGER FIELDS

M#-U#: M-number plus unit number
U-top: U-top-EL:
U-bot: U-bot-EL:

APPENDIX II

Document 12

*UNIT Database Field Names and Explanations

The following list contains the explanations of the typically abbreviated field names used in *UNIT databases in the File Module of Q&A®. The unabbreviated form of the field name is given parenthetically, followed by an explanation and/or examples of entry input to show the appropriate type of field information and style. This explanatory information is available to the Q&A® user through customized HELP fields while inputting or editing data. The fields are ordered as per row in *MNOS databases (see Appendix Document 4.2.1 for example).

Mno (M-number)

EERC MMRRRI section or geological observation number (e.g., M1000, M2345a). If this M-number entry (of the first screen or page) is inadvertently changed, the M-number entry of the second screen is not affected.

REF (Reference)

Primary reference information; examples of preferred formats: Hares (1928), Hartman (1986u), Hartman (1991u, v. 12) [u = unpublished]; U.S. Geological Survey OFR (for Open-file Reports); North Dakota Geological Survey; North Dakota State Water Commission.

DATE (Date of reference)

The date of the reference (REF) (e.g., 1978). Enter also the month and day if the reference is unpublished and the information is available (e.g., 1978/10/12).

SC (Section type)

Enter one of the following: DH = drill hole, MS = measured section, CS = coal section.

PAG (Pagination)

Secondary reference information. For typical references, enter pagination, such as page (p.), plate (pl.), etc. The letters "m" and "p" adjacent to page numbers stand for "map" and "photo" (the pagination "p. 34p, 35, 36m" indicates that a photo and map of the section is found on pages 34 and 36, respectively). For drill holes use this line for source of information, such as "NCRDS summary form," "drilling form," etc.

LOG

Represents data of first or subsequent revisions of M-number data on computer. The date is automatically entered in the ADD mode when entering data to a new form. Major revisions to a previous form should receive a new date. Save an old form as a hard copy or as secondary forms (non-"P" forms).

ST (State or Canadian Province)

Enter the two-letter designation for the state or province as per U.S. Postal standards.

REG (Region)

General regional areas include the Williston Basin (WB), Crazy Mountains Basin (CMB), Powder River Basin (PRB), Big Horn Basin (BHB). Most regions are further subdivided as follows: WB-LMR (WB-Little Missouri River), WB-FTU (WB-Fort Union), CMB-E (CMB-eastern), etc.

PJC (Project code)

A brief project-specific code can be entered for specialized sorts (e.g., "Slope," for Slope County area project).

mod (Form modification) See DATE and TIME of Last Modification.

(DATE of Last Modification)

If ANY changes are made to this form, the date that those changes were made will automatically be entered in this field. The DATE field is otherwise invisible.

(TIME of Last Modification)

If ANY changes are made to this form, the time that those changes were made will automatically be entered in this field. The TIME field is otherwise invisible.

ent (Enterer)

Initials of the person filling out the form.

U# (Unit number)

Surface sections are measured from the bottom up with ascending unit numbers. Subsurface sections are measured from the top down with descending numbers.

M#+U# (M-number + unit number)

The addition of these two numbers produces a unique number for each form. This value is entered automatically.

O (Original units of measure)

Enter "ft" or "m" to indicate in what units the original section was measured.

BED (Bed or unit name)

The name of the bed or unit represented by this data form. Use initials to reference the person making the interpretation (e.g., Harmon coal-CRS, HT Butte clinker-AGL).

DV (Divisions)

Enter the number of inches originally reported, or enter the number of divisions measured from the original drawing of the section. This value will be multiplied by the conversion factor (field x) to produce a value in feet, which will be added to the value in field + to produce the total unit thickness (TK/ft).

x (Multiplication factor)

Used with divisions to convert to feet.

SCALE

Scale or ruler used to determine unit thickness (e.g., 60 div/inch).

FM (Formation)

The name of the formation in which this unit occurs. Use initials to reference the person making the interpretation, e.g., Bullion Creek-CRS, Tongue River-AGL.

+ (Addition of integer)

This field usually represents feet as given in the original source. The divisions from the field DV are converted to feet and added to this field to give total number of feet (e.g., 4 ft, 3 inch = 3 inch x conversion + 4 ft = TK/ft).

COM (Comment)

Comment on stratigraphy.

TK/ft (Unit thickness in feet)

If the section thickness was originally measured in meters, leave this field blank. Conversion from the TK/m field will fill this field automatically.

SC-EL/Top (Elevation in feet at top of section)

Enter, in feet, the elevation of the top of the section.

SC-TK/ft (Total thickness of section in feet)

Enter, in feet, the total thickness of the section. If the section thickness was originally measured in meters, leave this field blank. Conversion from the field SC-TK/m will fill this field automatically.

Lnos (L-numbers)

Enter the L-numbers of the fossil localities that occur in this unit.

TK/m (Unit thickness in meters)

Enter, in meters, the thickness of the unit. The metric value will be automatically converted to feet and entered in the field TK/ft.

SC-EL/Bot (Elevation in feet at bottom of section)

Enter, in feet, the elevation of the bottom of the section.

SC-TK/m (Total thickness of section in meters)

Enter, in meters, the thickness of the section. This field is automatically calculated if the thickness in feet is entered in the field SC-TK/ft.

RK-S (Rock sample)

Enter the rock sample numbers or other sample collection numbers that apply to this unit.

DESC (General unit description)

Enter the general description of the unit. Wherever possible, quote the original description of section unit.

STRATCOL-LITH (STRATCOL lithic description)

Enter a lithologic description abbreviation used by the program STRATA/STRATCOL (e.g., sh, sh/silty, sh/carb, sh/calc, ss, ss/silty, etc.). Choose available entries from a field restriction value table (alt F7).

SYMBOL (STRATA/STRATCOL graphic symbol)

A symbol code represents the graphic pattern to be used to illustrate a lithologic description for a particular unit. This code is determined in the STRATA/STRATCOL program, and the value is entered automatically upon leaving the STRATCOL-LITH field.

RESISTANCE VALUE (Resistance to weathering)

This value is used in the STRATA/STRATCOL program to produce a weathering profile based on a preset determination of resistance for a particular lithology. This field is entered automatically upon leaving the field STRATCOL-LITH.

LITHOLOGY

Primary rock type (keyword) (e.g., claystone, siltstone, sandstone, etc.). Choose available entries from a field restriction value table (alt F7).

modifier (Rock type modifier)

Enter a lithic term, if necessary, to describe more accurately the unit lithology (e.g., silty, sandy, carbonaceous, etc.). Choose available entries from a field restriction value table (alt F7).

COLOR (Color of bed)

Enter the GSA color term (if possible) for the primary color of the unit. A color term will be automatically entered if the appropriate value is inputted in GSACOLOR field.

FRESH/DRY

Enter "F" or "D" to describe whether the color of the rock or sediment was determined from a fresh (F) or dry (D) sample.

GSACOLOR (GSA color code)

Enter the appropriate GSA color code (e.g., 5 Y 2/5). A descriptive color term will automatically be entered in the field color if GSACOLOR is entered.

NUM (Color index)

The NUM field represents an attempt to describe or differentiate colors based on a numerical system. This approach is experimental. A color index value is automatically entered if a color has been entered in the field GSACOLOR.

COLOR(COM) (Color comment)

This field is for an extended color description.

SEQU (Sequencing)

If applicable, enter apparent grain size trends within the unit (e.g., F-UP = fining upward; C-UP = coarsening upward).

S/S (Sedimentary structures)

If present, enter the names of the evident sedimentary structures.

Mno (M-number)

The M-number for this form is automatically entered on this page (screen) in the ADD mode. If the M-number on the first screen (page) is inadvertently changed, the M-number of the second screen is not affected.

REF (Reference)

The primary reference information for this form is automatically entered on this page (screen) in the ADD and UPDATE mode.

F-ENVIR (Fossil environments)

Enter the environment indicated by fossils (e.g., brackish, freshwater, terrestrial, marine, etc.).

S-ENVIR (Sedimentary environments)

Enter (briefly) the environment indicated from a sedimentological interpretation. Additional comments can be entered in field COM2.

COM2 (Comments)

Enter additional comments on the sedimentary environments represented in the unit.

SECTION STRUCTURAL INFORMATION BOX**fct (Function)**

Enter the appropriate trigonometric function (e.g., T = tangent, S = sine).

DIP

Enter the dip (in degrees) of the strata.

DIPrad

Dip in radians is automatically entered upon exiting the field DIP.

PACE

Enter the (walking) pace (length) used to calculate the horizontal (surface) distance.

fctval (Function value)

The trigonometric value for the function entered in field fct is automatically entered upon exiting field fctval.

SURF (Surface distance)

Enter the map surface distance used for structural calculations for a particular unit.

U-TK (Unit thickness)

This value is derived from trigonometric calculations using surface distance and dip.

SURF-T (Surface total)

Enter the total surface distance for the section.

SC-TK (Section thickness)

The total section thickness is derived using trigonometric functions using measured dips and surface distances.

NCRDS SPECIFIC FIELDS BOX

UQ (Unit qualifier)

Enter NCRDS unit qualifiers code (see list).

priLITH (Primary lithology)

Enter primary lithology from the NCRDS restricted value field table (alt F7).

modLITH (Modifying lithology)

Enter the lithic modifier from the NCRDS restricted value field table (alt F7). The lithic modifier is a one-word descriptive modifier of the primary lithology.

COLOR

Use GSA international standard color (**GSACOLOR**) abbreviation if available (e.g., 10YR7-4; do not use "/" as is traditionally used [10YR7/4]). Otherwise enter color from restricted value field table (alt F7).

GRsize (Grain size)

Enter the Wentworth-scale grain size.

GRshape (Grain shape)

Enter the grain shape (see NCRDS list of available codes).

MINERALS (Mineralogy)

Enter the mineral name from the NCRDS list of available codes.

BEDDING

Enter the bedding name from the NCRDS list of available codes.

CONTACT

Enter the contact type from the NCRDS list of available codes.

FOSSILS

Enter the fossil type from the NCRDS list of available codes.

FRACTURES

Enter the "F" to indicate presence of fractures.

JOINTS

Enter the "J" to indicate presence of fractures.

CLEATS

Enter the "C" to indicate presence of cleats.

WILD1 (Wild Card 1)

Wild Card 1 is a user-defined field.

WILD2 (Wild Card 2)

Wild Card 2 is a user-defined field.

COMMENT (Comment 2)

User-defined comment field.

STRATIFACT/LOG FIELDS BOX**M#-U# (combined M-number and unit number)**

A combined M-number and unit number produces a unique number for each form within the *UNIT database and can be used in other programs such as STRATIFACT.

U-top (unit top)

Enter the relative position (footage or metric value) of the unit top.

U-bot

Enter the relative position (footage or metric value) of the unit bottom.

U-top-EL

Enter the elevation (footage or metric value) of the unit top.

U-bot-EL

Enter the elevation (footage or metric value) of the unit bottom.

APPENDIX III

Document 13

*LOC Database Form (Q&A® File Module)

Lno: REF: DATE:
 P: PAG: LOG:
 ent: mod: (Date) (Time) UNQ:
 FY: refBOSS: from: FS: U: U:
 OFno: NAME:
 REF#: 24K: 100K:
 INST: #1: #2:

NAT: REG: FIELD: ldg: I#: O:
 ST: CO: QD: YR: SR: CI:
 QQ: SEC: T: NS: R: EW: SC: TC: RC:
 ELEV: +/-: INT-v S/: LG: LT:
 EL/m: +/-: X: gd: gm: gs: td: tm: ts:
 ftNS: #3: ftEW: #4: Z: Ng: UTM: Eg: UTM:
 mNS: #5: mEW: #6: CNS: CO1: CEW: CO2:

LOC:

End of first
screen

SE: ST: FM: MB: LEVEL:
 CTc: ftC: CT: mC: S: A:
 H1c: ft1: H1: m1: F: L:
 H2c: ft2: H2: m2:

V: ABV-B/ft: FM(ORG):
 W: BLW-T/ft: CCRES:

M#: U#: Proj XS: CL:

STRAT:

End of second
screen

COM:

SLD: PRT:

FAUNA:

***LOC Database Form, continued
(Q&A® File Module)**

**End of third
screen**

: :

D/YR: M/D: DISC:

D/COM:

CHIEF: of:
CYR: M-D: COLLR:

COLLR/COM:

COLLN: C/INST:
COLLN/COM:

**End of fourth
screen**

IDER:-----
: :
IDS

APPENDIX III

Document 14

*LOC Database Form with Data (Q&A® File Module)

Lno: L1127 REF: Hartman (1988u, v. 14) DATE: 1988/11/08
 P: P PAG: p. 93, 94m, 97m, 98-101, 102p, 103p, 104 LOG: 1990/10/30
 ent: JHH mod: UNQ: L1127P
 FY: 88f refBOSS: Hartman, J.H. from: UND-EMRC-MMRI
 OFno: CJH11-33 (Ostrea), CJH28-F FS: B U: S U:
 REF#: WB88-L1127 NAME:
 INST: USGS #1: Mz 07419 #2: 24K: Y 100K: Y

NAT: USA REG: WB-LMR FIELD: Slope-E3-01 ldg: 46103 I#: D7 O: m
 ST: ND CO: Slope QD: Boyce Creek West YR: 1980 SR: 7.5 CI: 20
 QQ: SW NE SW SE SE SEC: 13 T: 134 NS: N R: 105 EW: W SC: TC: RC:
 ELEV: 2952.0 +/-: 5 INT-v S/: LG: LT:
 EL/m: 899.8 +/-: : JHH X: gd: gm: gs: td: tm: ts:
 ftNS:N #3: 400 ftEW:W #4: 950 Z: Ng: UTM: Eg: UTM:
 mNS:N #5: 122 mEW:W #6: 290 CNS: CO1: CEW: CO2:

LOC: The outcrop of the oysters is somewhat less than about half of the
 outline of the knoll as outline on the topographic map. The shells probably
 occur from 10-12 ft above the contour line. Two shell horizons may be
 present; the lower one, however, appears interpretable as a reworked
 accumulation as it appears to be found only in alluvium and is not present lat

: L1127 : Hartman (1988u, v. 14)

SE: PAL ST: FM: Cannonball MB: upper tongue? LEVEL:

CTc: ftC: CT: mC: S: E1A A:
 H1c: 09 ft1: 85.0000 H1: T Cross lignite m1: 25.9083 F: T2 L:
 H2c: ft2: H2: m2:

V: ABV-B/ft: ABV-B/m: FM(ORG): Lance (Ostrea)
 W: BLW-T/ft: BLW-T/m: CODES:

M#: M1785 U#: 012 Project: XS: CL:

STRAT: The locality is 80-90? ft above the T Cross coal bed of Hares (comment
 on plane table sheet suggests coal originally thought to be the Beta coal
 bed) and 20-40? ft below the Ives coal of Hares (thought to be the Yule
 according to Hares). Water-worn siliceous pebbles and cobbles form a lag on
 the surrounding land surface; much sulfur and selenite occur in described
 portion of section and in the underlying undescribed strata.

: L1127 : Hartman (1988u, v. 14)

COM: There is no doubt that this oyster locality is equivalent to L1127 of
 Hares. The site was shown to me by Mr. Oldis, who is the current property
 owner, who in turn was shown the locality by Charlie Frerck, who told Oldis
 that the shells were used for chicken feed in homesteading days. Mr. Oldis
 drove us to the locality.

SLD: P9029-P9036

PRT: C1006-C1012

FAUNA: The locality consists exclusively of oysters. The oysters are
 predominantly (if not exclusively) exfoliated and broken. The living
 position may be indicated for some specimens, but in general the shells
 appear jumbled.

***MNOS Database Form with Data (continued)**
(Q&A® File Module)

: L1127 : Hartman (1988u, v. 14)

DYR: 1911 M/D: 10/ DISC: Price, W.A., Jr.

D/COM:

CHIEF: Hartman, J.H. of: UND-EERC-MMRI

CYR: 1988 M-D: 11/08 COLLR: Hartman, J.H., Hartman, J.L.

COLLR/COM:

COLLN: Y C/INST: USNM-I/USGS, UND-EERC

COLLN/COM:

IDER: Stanton

: L1127 : Hartman (1988u, v. 14)

IDS *Ostrea glabra*

APPENDIX III

Document 15

*LOC Database Form (Q&A® Write Module)

WILLISTON BASIN FOSSIL LOCALITY FORM

Joseph H. Hartman, UND-EERC-MMRRI

data entered on: ; form printed on: 1992/01/17

Locality Example

FOSSIL CATEGORIES:

REFERENCE :
REFERENCE BOSS :
REFERENCE # :
ORIGINAL FIELD# :
INSTITUTION # :

LOCALITY NAME :

INSTITUTION # :

LOCALITY LOCATION DATA

GENERAL LOCATION : , , County. STUDY AREA: region, field area
QUADRANGLE DATA : Quad., , series, foot contour interval (map location: ,)
LEGAL LOCATION : sec. , T. , R. . (section code:) (X-code:)
FROM SECTION LINE : feet , feet ; meters , meters
ELEVATION (ft/m) : +/- feet; +/- meters; INTERPRETER:
SITE DESCRIPTION :

STRATIGRAPHIC DATA

SERIES : STAGE :
FORMATION : ORIGINAL FORMATION :
MEMBER : ABOVE BASE of FM : feet meters
LEVEL IN FM : BELOW TOP of FM : feet meters
M-number (unit)
CONTACT : CT: feet CT: meters code:
HORIZON 1 : H1: feet H1: meters code:
HORIZON 2 : H2: feet H2: meters code:
HORIZON CODES :
STRATIGRAPHIC DESCRIPTION :

GENERAL LOCALITY COMMENTS

SLIDES : PRINTS :

DISCOVERY AND COLLECTING HISTORY

DISCOVERY : ().
DISC COMMENT :
COLLECTOR(S) : ().
COLLR COMMENT :
COLLN COMMENT :
REPOSITORIES :
ASSEMBLAGE :

IDENTIFICATIONS BY

APPENDIX III

Document 16

*LOC Database Example (Q&A® Write Module)

WILLISTON BASIN FOSSIL LOCALITY FORM

Joseph H. Hartman, UND-EERC-MMRI

data entered on: 1990/10/30; form printed on: 1992/01/17

Locality L1127

FOSSIL CATEGORIES: B

REFERENCE : Hartman (1988u, v. 14), p. 93, 94m, 97m, 98-101, 102p, 103p, 104
REFERENCE BOSS : Hartman, J.H., UND-EMRC-MMRI
REFERENCE # : WB88-L1127
ORIGINAL FIELD# : CJH11-33 (Ostrea), CJH28-F LOCALITY NAME :
INSTITUTION # : USGS Mz 07419 INSTITUTION # :

LOCALITY LOCATION DATA

GENERAL LOCATION : USA, ND, Slope County. STUDY AREA: WB-LMR region, Slope-E3-01 field area
QUADRANGLE DATA : Boyce Creek West Quad., 1980, 7.5 series, 20 foot contour interval (map location: 46103, D7)
LEGAL LOCATION : SW NE SW SE SE sec. 13, T. 134 N., R. 105 W. (section code:) (X-code:)
FROM SECTION LINE : 400 feet N, 950 feet W; 122 meters N, 290 meters W
ELEVATION (ft/m) : 2952.0 +/- 5 feet; 899.8 +/- meters; INTERPRETER: JHH
SITE DESCRIPTION : The outcrop of the oysters is somewhat less than about half of the outline of the knoll as outline on the topographic map. The shells probably occur from 10-12 ft above the contour line. Two shell horizons may be present; the lower one, however, appears interpretable as a reworked accumulation as it appears to be found only in alluvium and is not present laterally in exposed section. The locality is west-facing, at head of minor drainage forming the east flank of knoll.

STRATIGRAPHIC DATA

SERIES : PAL STAGE :
FORMATION : Cannonball ORIGINAL FORMATION : Lance (Ostrea)
MEMBER : upper tongue? ABOVE BASE of FM : feet meters
LEVEL IN FM : BELOW TOP of FM : feet meters
M-number : M1785 (unit 012)
CONTACT : CT: feet CT: meters code:
HORIZON 1 : T Cross lignite H1: 85.0000 feet H1: 25.9083 meters code: 09
HORIZON 2 : H2: feet H2: meters code:
HORIZON CODES :

STRATIGRAPHIC DESCRIPTION : The locality is 80-90? ft above the T Cross coal bed of Hares (comment on plane table sheet suggests coal originally thought to be the Beta coal bed) and 20-40? ft below the lvs coal of Hares (thought to be the Yule according to Hares). Water-worn siliceous pebbles and cobbles form a lag on the surrounding land surface; much sulfur and selenite occur in described portion of section and in the underlying undescribed strata.

GENERAL LOCALITY COMMENTS

There is no doubt that this oyster locality is equivalent to L1127 of Hares. The site was shown to me by Mr. Oldis, who is the current property owner, who in turn was shown the locality by Charlie Frerck, who told Oldis that the shells were used for chicken feed in homesteading days. Mr. Oldis drove us to the locality.

SLIDES : P9029-P9036 PRINTS : C1006-C1012

DISCOVERY AND COLLECTING HISTORY

DISCOVERY : 1911 (10/), Price, W.A., Jr.
DISC COMMENT :
COLLECTOR(S) : 1988 (11/08), Hartman, J.H., Hartman, J.L.
COLLR COMMENT :
COLLN COMMENT :
REPOSITORIES : USNM-I/USGS, UND-EERC
ASSEMBLAGE : The locality consists exclusively of oysters. The oysters are predominantly (if not exclusively) exfoliated and broken. The living position may be indicated for some specimens, but in general the shells appear jumbled.

IDENTIFICATIONS BY Stanton

Ostrea glabra

APPENDIX III

Document 17

*LOC Database Fields Organized by Topic (Q&A® File Module)

See Document 18 for full Field Names and Explanations

REFERENCE RELATED INFORMATION

Numbering Systems Fields

Lno:
OFno:
REF#:
INST: #1: #2:

Reference (Citation) Fields

REF:
PAG:
refBOSS: from:
NAME:
M#: U#:
COM:
SLD: PRT:

Record Management Fields

DATE:
P:
LOG:
ent:
mod: Last Date and Time of form modification
UNQ:
FY:
FS:
U: U: (utility fields)
24K: 100K:
O: (original unit of measure)
Project: XS: CL:

Screen Management Fields

[Lno]: [REF]: (for screens 2, 3, 4, and 5)

LOCATION FIELDS

General Location

NAT: ST: CO:
REG: FIELD:
QD: YR: SR: CI: ldg: I#:

***LOC Database FIELDS ORGANIZED BY TOPIC, continued**

LOCATION FIELDS, continued

Legal Location

QQ: SEC: S/: SC: T: NS: TC: R: EW: RC:
ftNS: #3: ftEW: #4:
mNS: #5: mEW: #6:
X:

Longitude and Latitude Coordinates

LG: LT:
gd: gm: gs: td: tm: ts:
X:

UTM Coordinates

Z: Ng: UTM: Eg: UTM:
X:

State Land Grid Coordinate System

CNS: C01: CEW: C02:
X:

Elevation Data

ELEV: EL/m:
+/-: +/-:

STRATIGRAPHY FIELDS

Chronostratigraphy

SE: S: ST: A: (series; stage)

Lithostratigraphic Nomenclature

FM: MB: LEVEL: F: L:
FM(ORG):

Horizon Data

CTc: ftC: CT: mC: (extraformational contact)
H1c: ft1: H1: m1: (intraformational horizon)
H2c: ft2: H2: m2: (intraformational horizon)
V: ABV-B/ft: ABV-B/m: (above base of formation)
W: BLW-T/ft: BLW-T/m: (below top of formation)
CODES: (stratigraphic thickness codes)
STRAT:

***LOC Database FIELDS ORGANIZED BY TOPIC, continued**

PALEONTOLOGY FIELDS

Fossil Data Management Fields

FS:

Discovery Data

DYR: M/D: DISC: D/COM:

Collection Data

CHIEF: of:
CYR: M-D: COLLR: COLLR/COM:
COLLN: C/INST: COLLN/COM:

General Faunal Comments

FAUNA:

Fossil Identifications

IDER: IDS:

APPENDIX III

Document 18

*LOC Database Field Names and Explanations

The following list contains the explanations of the typically abbreviated field names used in *LOC databases in the File Module of Q&A®. The unabbreviated form of the field name is given parenthetically, followed by an explanation and/or examples of entry input to show the appropriate type of field information and style. This explanatory information is available to the Q&A® user through customized HELP fields while inputting or editing data. The fields are ordered as per row in *MNOS databases (see Appendix Document 4.3.1 for example).

Lno (L-number)

The **L-number** represents a paleontological locality numbering system initiated and maintained by Joseph H. Hartman. If this L-number entry (of the first screen or page) is inadvertently changed, the L-number entry of the second and subsequent screens is not affected.

REF (Reference)

Examples of preferred reference formats: Hares (1928), Hartman (1986u), Hartman (1991u, v. 12) [u = unpublished]; U.S. Geological Survey OFR (for Open-file reports); North Dakota Geological Survey; North Dakota State Water Commission. The primary reference information for this form is automatically entered on the second and subsequent pages (screens) in the ADD and UPDATE mode.

DATE (Date of reference)

The date of the reference (**REF**) (e.g., 1978). Enter also the month and day if the reference is unpublished and the information is available (e.g., 1978/10/12).

P (Primary form)

Enter "P" for all primary forms. Leave empty for all other (duplicate = other use) forms.

PAG (Pagination)

Secondary reference information. For typical references, enter pagination, such as page (p.), plate (pl.), etc. The letters "m" and "p" adjacent to page numbers stand for "map" and "photo" (the pagination "p. 34p, 35, 36m" indicates that a photo and map of the section is found on pages 34 and 36, respectively). For drill holes use this line for source of information, such as "NCRDS summary form," "drilling form," etc.

LOG

Represents data of first or subsequent revisions of L-number data on computer. The date is automatically entered in the ADD mode when entering data to a new form. Major revisions to a previous form should receive a new date. Save an old form as a hard copy or as secondary forms (non-"P" forms).

ent (Enterer)

Initials of person who is responsible for filling in form. Note any interpretations (location information, etc.) on page 2 of form under STRAT, LOC, or COM. Note also INT, this field represents the interpretation of elevations (if differing from original).

mod (Form modification) See DATE and TIME of Last Modification.

(DATE of Last Modification)

If ANY changes are made to this form, the date that those changes were made will automatically be entered in this field. The "Date of modification" field is otherwise invisible.

(TIME of Last Modification)

If ANY changes are made to this form, the time that those changes were made will automatically be entered in this field. The "Time of modification" field is otherwise invisible.

UNQ (Unique L-number)

This field is automatically entered combining fields Lno and P to make LnoP (e.g., L1002P). The purpose of this addition is to create a unique L-number for external lookup files.

FY (Field year and project)

Enter the field year of the project and a letter code for the project (e.g., 90a). The project letter code is consecutive for the year (i.e., "a" would be the first project for 1990 and corresponds to the travel file designations).

refBOSS (Reference boss)

Enter the last name and initials of person in charge of reference (e.g., Hares, C.J.). This entry may be the same as in field REF.

from

Enter the institution of the refBOSS (e.g., University of North Dakota, U.S. Geological Survey, North Dakota Geological Survey).

OFno (Original field number)

Enter the number originally applied to the locality. This number is usually the number (or name) assigned to the locality at the time of discovery during field work.

FS (Taxon categories)

Enter the letter codes for the taxon categories represented at the locality, maintaining the order INOBVMTPL. The codes are as follows: I = invertebrates (misc.); N = nonmarine mollusks; O = marine mollusks; B = brackish mollusks; V = non-mammalian vertebrates; M = mammals; P = plants; T = microsites; L = lithic samples.

U (Utility field 1)

This is a user-defined field for project sorts.

U (Utility field 2)

This is a user-defined field for project sorts.

REF# (Reference number)

The reference number is a number applied to the locality in the reference. This number may or may not be the original field number (OFno). If the field number (OFno) and the reference number (REF#) are the same for a particular reference (REF), they should both be inputted.

NAME (Name of locality)

Enter the name of the locality used by the reference.

INST (Institution acronym)

If assigned, enter the standard institutional acronym applied to the numbering system used for this locality (e.g., USNM-I). Do not enter an institutional acronym if no locality number is known or assigned.

#1 (Institutional locality number)

For a USGS number, enter Mz ####, Cz ####, or other appropriate number and system designation. If a USGS locality was assigned both Mz and Cz numbers, enter the Mz number in this field.

#2 (Additional institute or reference number)

If a USGS locality was assigned both Mz and Cz numbers, enter the Cz number in this field.

24K

Enter "P" if the locality has been plotted on 1:24,000-scale map.

100K

Enter "P" if the locality has been plotted on 1:100,000-scale map

NAT (Nation)

Enter a three-letter abbreviation for the nation of the locality (e.g., USA, CAN).

REG (Region)

Enter a regional designation for the locality. These designations are predetermined; examples for the Williston Basin are as follows: WB-NDC = central North Dakota; WB-LMR = Little Missouri River; WB-FTU = Fort Union; WB-W = Garfield and McCone Counties; WB-N = northern Montana; WB-SK = Saskatchewan.

FIELD (Field or study area)

Enter the name of the field or study area (if available) in which the locality occurs (e.g., Williston lignite field, Charlson oil field). The field area is an area smaller than a region (REG) and generally is an area designated by the reference (REF).

1dg (1 degree)

Enter the 1 x 1-degree reference number cited by the USGS in state quadrangle booklets (automatically entered after leaving field QD).

I# (Map index number)

Indexes quadrangles within 1 x 1-degree areas by the USGS methods. This field is automatically filled upon leaving the QD field.

O (Original units of measure)

Enter "ft" or "m" to indicate in what units the original locality was measured.

ST (State)

Enter the two-letter designation for the state or province as per U.S. Postal standards.

CO (County)

Enter the name of the county in which the locality occurs.

QD (Quadrangle)

Enter the name of the USGS 7.5-minute quadrangle on which the locality is located.

YR (Year quadrangle was published)

This field is automatically filled upon leaving the QD field.

SR (Map series)

7.5' = 1:24,000; 15' = 1:62,500 (not typically used). This field is automatically filled upon leaving the QD field.

CI (Contour interval)

The contour interval for all 7.5' maps is presently in feet. This field is automatically entered upon leaving the QD field (if the data has been inputted in the MAPS database).

QQ (Quarter section subdivisions)

Enter the quarter section subdivision (e.g., SW SE NW) for the location of the locality. Use other descriptive terms as necessary, e.g., C west edge (C = center); near; about; central.

SEC (Section)

Enter the section number in which the locality occurs. If the locality occurs in more than one section (as with a quarry, for example), place the appropriate code in the field SC.

T (Township)

Enter the township number in which the locality occurs (e.g., 124). Enter the number only. Do not enter the preceding "T" or the subsequent "N" or "S."

NS (North/South)

Enter N or S in reference to townships north or south of the base line.

R (Range)

Enter the range number in which the locality occurs (e.g., 84). Enter the number only. Do not enter the preceding "R" or the subsequent "E" or "W."

EW (East/West)

Enter E or W in reference to townships east or west of the principal meridian.

SC (Section code)

Enter "?" if there is uncertainty in the section designation (used primarily for historical records with inspecific data). Enter "/" if a locality occurs in more than one section, and enter this additional section in the field S/.

TC (Township code)

Enter "?" if there is uncertainty in the township designation (used primarily for historical records with inspecific data). Enter 2pm (2nd principal meridian), 3pm (3rd principal meridian), etc., for reference to Canadian principal meridians.

RC (Range code)

Enter "?" if there is uncertainty in the range designation (used primarily for historical records with inspecific data).

ELEV (Elevation in feet)

Enter the elevation (in feet) of the locality. If the elevation was originally entered in meters, leave this field blank. The conversion from meters to feet will be done automatically upon leaving the field EL/m.

+/- (Elevation accuracy in feet)

Enter the letters "A" (= approximate) or "vA" (= very approximate) as estimates of the locality's elevation, or enter the footage value based on an interpretation of contours on a topographic map (e.g., "10" = +/- 10 ft).

INT (Interpreter of elevation)

Enter the initials of person making the interpretation of the elevation.

S/ (Additional township and range section number)

Enter the additional section number (e.g., 24) in which the locality occurs. This section is in reference to the section number given in field SEC.

LG (Longitude)

Enter longitude of the locality in the following format: ###.####.

LT (Latitude)

Enter the latitude of the locality in the following format: ##.####.

EL/m (Elevation of locality in meters)

Enter the elevation of the locality in meters if originally measured in meters. This value will automatically be converted to feet in the field ELEV.

+/- (Elevation accuracy in meters)

Enter the letters "A" (= approximate) or "vA" (= very approximate) as estimates of the locality's elevation, or enter the metric value based on an interpretation of contours on a topographic map (e.g., "3" = +/- 3 m).

X (Coordinate location code)

Enter "X" to indicate that the coordinate system location was based on an arbitrarily plotted point (where the locality was only known to an area).

gd (Longitude value for degrees)

This value is automatically extracted from the longitude value.

gm (Longitude value for minutes)

This value is automatically extracted from the longitude value.

gs (Longitude value for seconds)

This value is automatically extracted from the longitude value.

td (Latitude value for degrees)

This value is automatically extracted from the latitude value.

tm (Latitude value for minutes)

This value is automatically extracted from the latitude value.

ts (Latitude value for seconds)

This value is automatically extracted from the latitude value.

ftNS (Feet north or south of section line)

Enter "N" or "S" to indicate in which direction the distance from a section line was measured. This field is automatically filled if the metric value is entered in Field #5.

#3 (Number of feet north or south of a section line)

Enter the distance in feet north or south of a section line.

ftEW (Feet east or west of a section line)

Enter "E" or "W" to indicate in which direction the distance from a section line was measured. This field is automatically filled if the metric value is entered in Field #6.

#4 (Number of feet east or west of a section line)

Enter the distance in feet east or west of a section line.

Z (Zone of UTM coordinate system)

Enter the zone number (e.g., 12) for the following UTM coordinate.

Ng (Northing for UTM coordinate system)

This value is preset for northing (N).

UTM (Universal Transverse Mercator coordinate system northing number)

Enter the northing number; commas are automatically emplaced.

Eg (Easting for UTM coordinate system)

This value is preset for easting (E).

UTM (Universal Transverse Mercator coordinate system easting number)

Enter the easting number; commas are automatically emplaced.

mNS (Meters north or south of a section line)

Enter "N" or "S" to indicate in which direction the distance from a section line is measured. This field is filled automatically if **ftNS** is entered.

#5 (Number of meters north or west of a section line)

Enter the distance in meters north or south of a section line. This field is automatically filled if **#3** is entered.

mEW (Meters east or west of a section line)

Enter "E" or "W" to indicate in which direction the distance from a section line is measured. This field is filled automatically if **ftEW** is entered.

#6 (Number of meters east or west of a section line)

Enter the distance in meters east or west of a section line. This field is automatically filled if **#4** is entered.

CNS (North/south code)

As appropriate, enter "N" (north) or "S" (south) zone code for the 10,000-ft state plane coordinate system.

C01 (10,000-ft coordinate number)

Enter the 10,000-ft coordinate number appropriate for the location of the locality. This number is read from a USGS quadrangle (commas are applied to this number automatically).

CEW (East/west code)

As appropriate, enter "E" (east) or "W" (west) zone code for the 10,000-ft state plane coordinate system.

C02 (10,000-ft coordinate number)

Enter the 10,000-ft coordinate number appropriate for the location of the locality. This number is read from a USGS quadrangle (commas are applied to this number automatically).

LOC (Descriptive locality information)

This field contains a general description of the location of the locality. This information should be quoted from the reference (**REF**) whenever possible.

SE (Series)

Enter the series in which the locality occurs. In the northern Great Plains, one of the following abbreviations is most commonly used: UK = Upper Cretaceous, PAL = Paleocene, EOC = Eocene. Stage codes are automatically entered in the field **S** upon leaving the field **SERIES**.

ST (Stage)

Enter the stage in which the locality occurs. In the northern Great Plains, one of the following abbreviations is most commonly used for uppermost Cretaceous- and Paleocene-age localities: La = Lancian, BC = Bugcreekian (BCa, b, c); M = Mantuan (Ma, Mb); Pu = Puercan (Pu1, Pu2, Pu3); Torrejonian (To1, To2, To3a, b); Ti = Tiffanian (Ti1, Ti2, Ti3, Ti4, Ti5); Cf = Clarkforkian (Cf1, Cf2, Cf3). Stage codes are automatically entered in the field **A** upon leaving the field **STAGE**.

FM (Formation name)

Enter the name of the formation in which the locality occurs. The formation code is automatically entered in the field F upon leaving the field FM.

MB (Member name)

Enter the name of the member of the formation in which the locality occurs.

LEVEL

Enter the stratigraphic level of formation (or member) in which the locality occurs (e.g., undiff., basal, lower, middle, upper, top). The level code is automatically entered in field L upon leaving field LEVEL.

CTc (Code for extra-formational contact field CT)

Enter a project-specific code.

ftC (Feet relative to contact)

Enter the footage of the locality horizon relative to a specified contact (as entered in field CT). If below the horizon, prefix the number with "-", if above the horizon, do not use a prefix.

CT (Name of contact)

Enter the name of the formational contact (as applied to fields CTc, ftC, and mC (e.g., Bullion Creek/Sentinel Butte).

mC (Meters relative to contact)

Enter the meters of a locality horizon relative to a specified contact (as entered in field CT). If below the horizon, prefix the number with "-", if above the horizon, do not use a prefix.

S (Series code)

The series code is automatically entered after entering the epoch abbreviation in the field EP.

A (Stage code)

The stage code is automatically entered after entering data in the field STAGE.

H1c (Horizon code)

Like fields CTc and H2c, this field code is project-specific, and is a reference to the horizon entered in field H1. For example, the following codes are applicable to the "Slope Project": 1 = HLCK; 2a = blw Limber; 2b = blw Beta; 3 = Beta-T Cross; 4 = 1o CNBL; 5a = CNBL-LCP; 5b = btw LCP; 6a = Warwick; 6b = Wasko A; 6b = Wasko B; 6d = LCP-UCP; 7a = btw UCP; 7b = EYM; 8a = UCP-Oyster; 8b = WYM; 9 = up CNBL; 10 = CNBL-No. 1; 11 = No. 1-Yule; 12 = Yule-H; 13 = H-Harmon; 14 = Harmon-Meyer; 15 = Meyer-HT Butte.

ft1 (Feet relative to horizon 1)

Enter the footage above or below (-) horizon H1, indicating the relative position of the locality. Horizon 1 (H1) is a user-specified horizon.

H1 (Name of horizon 1)

Enter the name of the horizon to which the locality is referred (e.g., blue bed).

m1 (Meters relative to horizon 1)

Enter the meters above or below (-) horizon H1, indicating the relative position of the locality. Horizon 1 (H1) is a user-specified horizon.

F (Formation code)

The formation code will be entered automatically upon leaving the field FM. These values are used to order the formations stratigraphically. Use the field LEVEL to indicate the general level of the locality within a formation. Examples of field F codes are: 0 = Fort Union; 1 = Ludlow; 2 = Slope; 3 = Cannonball; 4 = Bullion Creek; 5 = Sentinel Butte.

L (Level code)

The level code will be entered automatically upon leaving the field LEVEL. Level stratigraphic codes are as follows: a = locality only known to formation; b = basal; c = lower; d = middle; e = upper; f = top; g = occurrence near the contact between the underlying formation and overlying formation (usually used in conjunction with overlying formation).

H2c (Horizon code)

Enter the user-specific horizon code (for horizon 2). See the field H1c for examples of horizon codes.

ft2 (Feet relative to horizon 2)

Enter the footage above or below (-) horizon H2, indicating the relative position of the locality. Horizon 2 (H2) is a user-specified horizon.

H2 (Name of horizon 2)

Enter the name of the horizon to which the locality is referred (e.g., white marker bed).

m2 (Meters relative to horizon 2)

Enter the meters above or below (-) horizon H2, indicating the relative position of the locality. Horizon 2 (H2) is a user-specified horizon.

V (Code field for ABV-B/ft and ABV-B/m)

Enter the following "standard" codes for consistency in reference to the numerical value entered in field ABV-B/ft or ABV-B/m: C = calculated; E = rough estimate; G = given; M = measured.

ABV-B/ft (Feet above base of formation)

Enter the number of feet the locality occurs above the base of a formation. Conversion to metric is done automatically upon leaving the field and is entered in ABV-B/m.

ABV-B/m (Meters above base of formation)

Enter the number of meters the locality occurs above the base of the formation. The conversion to feet is done automatically upon leaving the field and is entered in ABV-B/ft.

FM(ORG) (Original formation name used)

Enter the original formation to which the locality was assigned. This information is intended primarily to indicate previously used formation names for a locality occurrence. Add formation names as used in revisions or upgrades to a different formation name, or to clarify a particular usage.

W (Code field for BLW-T/ft and BLW-T/m)

Enter the following "standard" codes for consistency in reference to the numerical value entered in field BLW-T/ft or BLW-T/m: C = calculated; E = rough estimate; G = given; M = measured.

BLW-T/ft (Feet below top of formation)

Enter number of feet the locality occurs below the top of the formation. A conversion to metric units is done automatically and entered in BLW-T/m upon leaving field BLW-T/ft.

BLW-T/m (Meters below top of formation)

Enter the number of meters the locality occurs below the top of the formation. A conversion to feet is done automatically and is entered in BLW-T/ft upon leaving BLW-T/m.

CODES (Contact codes)

Enter one of the following contact codes: C = calculated; R = rough estimate; E = estimate; G = given; G-E = given estimate; M = measured.

M# (M-number)

Enter the (EERC MMRRI) M-number identifying a geologic section that includes the locality.

U# (Unit number)

Enter the unit number of a particular M-number that includes the locality.

Project (Field or zone project)

The project field represents a subdivision of the field REG, as used in Hartman (1984) for the location of cross sections panels and corresponds to the "zone" field area.

XS (Cross section or panel identifier)

Enter the number of the cross section in which the geologic section is illustrated in which the locality occurs.

CL (Column number)

Enter the number of the column occurring in the cross section referred to in field XS in which the locality occurs.

STRAT (Stratigraphy)

Enter general stratigraphic comments, quoting from the original reference whenever possible.

COM (Comment)

Enter general comments about the locality that do not seem to fit anywhere else.

SLD (Slides)

Enter the numbers of the slides taken of the locality (e.g., P1234) (P-numbers are Hartman slides).

PRT (Prints)

Enter the numbers of the prints taken of the locality (e.g., C1234) (C-numbers are Hartman prints).

FAUNA (Faunal comments)

Enter comments on the general nature and significance of the faunal assemblage at the locality.

DYR (Discovery year)

Enter the year the locality was discovered.

M/D (Month/day)

Enter the month and day the locality was discovered (e.g., 04/09).

DISC (Discoverer)

Enter the names of the discoverers of the locality (names only) in the following format: Hartman, J.H., Strait, S.G.

D/COM (Discovery comment)

Enter comments on how the locality was discovered.

CHIEF

Enter the name of the field crew chief responsible for the project (e.g., Hartman for CMF collection of nonmarine Mollusca, Krause for vertebrates, Collier for collections as part of the USGS field party activities).

of (Affiliation of the CHIEF)

Institutional affiliation of the "CHIEF" of field crew (overall boss of field work for a particular crew) (e.g., USGS).

CYR (Year of collection)

Enter the year(s) the locality was collected.

M-D (Month/day)

Enter the month and day the locality was collected (e.g., 09/21).

COLLR (Name of collectors)

Enter the name of the collectors (e.g., Peck, W.D., Kroeger, T.J.)

COLLR/COM (Comments on collectors)

Enter comments on collection history in reference to collectors.

COLLN (Collections)

Enter "Y" (yes) or "N" (no) for the existence of any collections at this locality (not in reference to a particular record).

C/INST (Institutional repository)

Enter the acronym for the institution maintaining the collections from the locality.

COLLN/COM (Collection comment)

Enter general comments on the nature of the collection (i.e., value of the specimens).

IDER (Identifier)

Enter the name of the identifier and date of identification. For office identifications use the following format: last name of identifier (year, month/day) (e.g., Hartman [1988, 04/05]). For published identifications use the following format: Last name of identifier and year of publication (e.g., Hartman [1976], Stanton [1909]).

IDS (Faunule for locality)

List the fossils identified from this locality.

APPENDIX IV

Geochemical Database Design

A Summary and Annotation of the Cenozoic Project Data compiled by LeFever and Murphy (1983)

Document 19

Notes on the usefulness of the Cenozoic Project data

1. In most cases, the source data is not specific enough (i.e., no page numbers or specific authors).
2. The location data is only a very rough estimate, often only to the nearest township or section (see example 3 of the GEOGRAPHIC-GEOLOGIC-BIBLIOGRAPHIC DATA).
3. Little or no stratigraphic or elevation control on the localities (see example 1 of the LITHOLOGIC DATA).
4. Some confusion was created when different locality numbers were assigned to the same drill hole or outcrop. There is some question as to whether each sample analysis should have its own identifying number or if each location (drill hole, outcrop) should have a unique identifier with the samples being a subset of these localities (i.e., 3476-A; 1209-C, etc.)
5. Examples 6 and 7 of the GEOGRAPHIC\GEOLOGIC\BIBLIOGRAPHIC DATA and their associated COAL CHEMISTRY forms were compiled to show examples of data which have geographic and stratigraphic control.

Document 20

Cenozoic Project Database Structure and Utility

Part 1

GEOGRAPHIC-GEOLOGIC-BIBLIOGRAPHIC DATA

Field data in example 1 is interpreted as follows (in field order): LOCALITY 2333 is located in Dunn County, North Dakota, in the SW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 15, T. 144 N., R. 94 W, in the Dunn-Center coal field. LOCALITY 2333 represents a drill hole in the Fort Union Formation of the Paleocene Series of the Tertiary System. The "C" in the "ODS2" field indicates there is coal chemistry data available in that data file. The "Y" in the "ODATA" field indicates there is additional data in the source which was not utilized. The source for this data is given as the U.S. Geological Survey Open-File Report 78-1078, printed in 1978. The latitude and longitude are rough estimates derived from a computer program designed by Richard D. LeFever. The program utilizes the township and range data to calculate the latitude and longitude. The "X" and "Y" values are the coordinates used by R.D. LeFever. The origin for the coordinate system is near the southwest corner of North Dakota and it is not associated with the State Plane Coordinates System.

Example 1

LOCALITY: 2333	ODS1:
STATE: ND	ODS2: C
COUNTY: DUNN	ODS3:
T: 144	ODS4:
NS: N	ODS5:
R: 94	ODATA: Y
EW: W	YEAR: 1978
SECTION: 15	SOURCE: USGS OFR
Q1: B	AUTHOR: 78-1078
Q2: D	
Q3:	LAT : 47.2917
FIELD: DUNN CTR	LONG: 102.58
FM: TFU	X: 8.747162
SYSTEM: TER	Y: 11.9906
SERIES: PAL	
DTYPE: H	

Part 1, continued
GEOGRAPHIC-GEOLOGIC-BIBLIOGRAPHIC DATA

Example 2

LOCALITY: 8385	ODS1: C
STATE: ND	ODS2:
COUNTY: BOWMAN	ODS3:
T: 131	ODS4:
NS: N	ODS5:
R: 99	ODATA: Y
EW: W	YEAR: 1968
SECTION: 34	SOURCE: USBM RI
Q1: A	AUTHOR: 7158
Q2: B	
Q3: A	LAT : 46.12326
FIELD: SCRANTON	LONG: 103.0442
FM: TTR	X: 6.088158
SYSTEM: TER	Y: 1.67903
SERIES: PAL	
DTYPE: S	

Example 3

LOCALITY: 2420	ODS1: L
STATE: ND	ODS2:
COUNTY: STARK	ODS3:
T: 138	ODS4:
NS: N	ODS5:
R: 99	ODATA: Y
EW: W	YEAR: 1980
SECTION:	SOURCE: USGS OFR
Q1:	AUTHOR: 80-870
Q2:	
Q3:	LAT : 46.76133
FIELD:	LONG: 103.1679
FM: TFU	X: 5.281125
SYSTEM: TER	Y: 7.27813
SERIES: PAL	
DTYPE: H	

Part 1, continued
GEOGRAPHIC-GEOLOGIC-BIBLIOGRAPHIC DATA

Example 4

LOCALITY: 2674	ODS1:
STATE: ND	ODS2: C
COUNTY: BOWMAN	ODS3:
T: 131	ODS4:
NS: N	ODS5:
R: 99	ODATA: Y
EW: W	YEAR: 1979
SECTION:	SOURCE: USGS OFR
Q1:	AUTHOR: 79-1698
Q2:	
Q3:	LAT : 46.15313
FIELD:	LONG: 103.0585
FM: TFU	X: 5.998381
SYSTEM: TER	Y: 1.940339
SERIES: PAL	
DTYPE: H	

Example 5

LOCALITY: 5667	ODS1: L
STATE: ND	ODS2:
COUNTY: SLOPE	ODS3:
T: 135	ODS4:
NS: N	ODS5:
R: 105	ODATA: Y
EW: W	YEAR: 1965
SECTION: 10	SOURCE: UMI DS
Q1:	AUTHOR: CVANCARA A
Q2:	
Q3:	LAT : 46.52239
FIELD:	LONG: 103.8537
FM: TL	X: 1.153893
SYSTEM: TER	Y: 5.153172
SERIES: PAL	
DTYPE: 0	

Part 1, continued
GEOGRAPHIC-GEOLOGIC-BIBLIOGRAPHIC DATA

Example 6

LOCALITY: FORS-LB2	ODS1: C
STATE: ND	ODS2:
COUNTY: Dunn	ODS3:
T: 148	ODS4:
NS: N	ODS5:
R: 95	ODATA:
EW: W	YEAR: 1985
SECTION: 34	SOURCE: UND DS
Q1: C	AUTHOR: FORSMAN
Q2: A	
Q3: C	LAT :
FIELD:	LONG:
FM: TSB	X:
SYSTEM: TER	Y:
SERIES: PAL	
DTYPE: 0	

Example 7

LOCALITY: M2077-1	ODS1: C
STATE: ND	ODS2:
COUNTY: WILLIAMS	ODS3:
T: 100	ODS4:
NS: N	ODS5:
R: 155	ODATA:
EW: W	YEAR: 1966
SECTION: 22	SOURCE: 1
Q1: C	AUTHOR: GNRWY
Q2: D	
Q3:	LAT :
FIELD: Avoca	LONG:
FM: TSB	X:
SYSTEM: TER	Y:
SERIES: PAL	
DTYPE: H	

Part 2 LITHOLOGIC DATA

The boxed areas in Part 2 contain the fields originally defined in the Cenozoic Project database (LeFever and Murphy, 1983). The fields to the right of the boxes were added to the Q&A® version of this database. The new fields allow the user to know, through relational database management, the reference and geographic (LOCALITY of Part 1) information relevant to the lithologic data. These fields are automatically filled by a programming statement that posts the data from the appropriate form in the GEOGRAPHIC-GEOLOGIC-BIBLIOGRAPHIC data file. The field titled "Coal chem data avail" is a "yes/no" field indicating whether there is a form for the particular LOCALITY in the COAL CHEMISTRY data file.

Example 1

LOCALITY: 2674			State: ND
TSECT:			County: BOWMAN
TOPELEV:			TWP: 131 NS: N
			RGE: 99 EW: W
NCG:	TCG:	COALNAME: HARMON	section:
NSS:	TSS:	COALOV:	Q1: Q2: Q3:
NSH:	TSH:	COALRES:	
NLS:	TLS:	CRTYPE:	
NCL:	TCL:	URRES:	Year: 1979
NCK:	TCK:	URTYPE:	Source: USGS OFR
MEAN:			Author: 79-1698
SD:			
DDTYPE:			Coal chem data avail: Y

Part 2, continued
LITHOLOGIC DATA

Example 2

LOCALITY: 2333		
TSECT:	TOPELEV:	
NCG:	TCG:	COALNAME: A
NSS:	TSS:	COALOV:
NSH:	TSH:	COALRES:
NLS:	TLS:	CRTYPE:
NCL:	TCL:	URRES:
NCK:	TCK:	URTYPE:
MEAN:		
SD:		
DDTYPE:		

State: ND
County: DUNN
TWP: 144 NS: N
RGE: 94 EW: W
section: 15
Q1: B Q2: D Q3:

Year: 1978
Source: USGS OFR
Author: 78-1078

Coal chem data avail: Y

Example 3

LOCALITY: 2420		
TSECT:	TOPELEV:	
NCG:	TCG:	COALNAME: HT BUTTE
NSS:	TSS:	COALOV:
NSH:	TSH:	COALRES: 2.13
NLS:	TLS:	CRTYPE: I
NCL:	TCL:	URRES:
NCK:	TCK:	URTYPE:
MEAN:		
SD:		
DDTYPE:		

State: ND
County: STARK
TWP: 138 NS: N
RGE: 99 EW: W
section:
Q1: Q2: Q3:

Year: 1980
Source: USGS OFR
Author: 80-870

Coal chem data avail: N

Part 2, continued
LITHOLOGIC DATA

Example 4

LOCALITY: 5667		
TSECT: 141.3		TOPELEV: 2867
NCG: 0	TCG: 0	COALNAME: LIGNITE
NSS: 11	TSS: 67.2	COALOV: 61.6
NSH: 14	TSH:	COALRES:
NLS: 0	TLS: 0	CRTYPE:
NCL: 7	TCL: 12.1	URRES:
NCK: 0	TCK: 0	URTYPE:
MEAN:		
SD:		
DDTYPE:		

State: ND
County: SLOPE
TWP: 135 NS: N
RGE: 105 EW: W
section: 10
Q1: Q2: Q3:

Year: 1965
Source: UMI DS
Author: CVANCARA A

Coal chem data avail: N

Part 3, continued
COAL CHEMISTRY DATA

The boxed areas in Part 3 contain the fields originally defined in the Cenozoic Project database (LeFever and Murphy, 1983). The fields to the right of the boxes were added to the Q&A® version of this database. The new fields allow the user to know, through relational database management, the reference and geographic (LOCALITY of Part 1) information relevant to the coal chemistry data. These fields are automatically filled by a programming statement that posts the data from the appropriate form in the GEOGRAPHIC-GEOLOGIC-BIBLIOGRAPHIC data file. The stratigraphic control fields are derived from the LITHOLOGIC data file and are included in this data file to allow the user to know if there is any stratigraphic control on the available coal chemistry.

Example 1

LOCALITY: 2674 RANK: LG STYPE: D ATYPE: 0 VALUES: 1 TRACE: N ODATA: N GRIND: BTU: 6110 DEFORM: SOFTEN: FLUID: FREESWL:	MOISTURE: 43 VOLATILE: 25 FCARBON: 7 ASH: 0.1 H: CARBON: OXYGEN: NITROGEN: SULFUR: 0.8 PYRSUL: ORGSUL: SULFATE:	State: ND County: BOWMAN TWP: 131 NS: N RGE: 99 EW: W section: Q1: Q2: Q3: Year: 1979 Source: USGS OFR Author: 79-1698 Stratigraphic control Top-El: Not given TK/Sec: Not given CoalOV: Not given
--	--	--

Part 3, continued
COAL CHEMISTRY DATA

Example 2

LOCALITY: 8385	MOISTURE: 44
RANK: LG	VOLATILE: 24
SType: 0	FCARBON: 25
ATYPE: 4	ASH: 7
VALUES: 0	H: 7.4
TRACE: Y	CARBON: 35.4
ODATA: Y	OXYGEN: 49
GRIND:	NITROGEN: 0.5
BTU: 5960	SULFUR: 0.9
DEFORM: 2060	PYRSUL: 0.3
SOFTEN: 2110	ORGSUL: 0.6
FLUID: 2130	SULFATE: 0
FREESWL:	

State: ND
County: BOWMAN
TWP: 131 NS: N
RGE: 99 EW: W
section: 34
Q1: A Q2: B Q3: A

Year: 1968
Source: USBM RI
Author: 7158

Stratigraphic control
Top-El: Not given
TK/Sec: Not given
CoalOV: Not given

Example 3

LOCALITY: FORS-LB2	MOISTURE:
RANK:	VOLATILE: 30.3
SType: 0	FCARBON:
ATYPE: 0	ASH: 21.6
VALUES: 0	H: 4.02
TRACE:	CARBON: 38.64
ODATA: Y	OXYGEN: 15.38
GRIND:	NITROGEN: 0.63
BTU: 6027	SULFUR: 0.63
DEFORM:	PYRSUL:
SOFTEN:	ORGSUL:
FLUID:	SULFATE:
FREESWL:	

State: ND
County: Dunn
TWP: 148 NS: N
RGE: 95 EW: W
section: 34
Q1: C Q2: A Q3: C

Year: 1985
Source: UND DS
Author: FORSMAN

Stratigraphic control
Top-El: Not given
TK/Sec: 310
CoalOV: 219.5

Part 3, continued
COAL CHEMISTRY DATA

Example 4

LOCALITY: M2077-1	MOISTURE: 40.17
RANK:	VOLATILE: 26.82
STYPE: D	FCARBON: 27.88
ATYPE: 0	ASH: 5.13
VALUES:	H:
TRACE:	CARBON:
ODATA:	OXYGEN:
GRIND:	NITROGEN:
BTU: 6644	SULFUR: 0.29
DEFORM:	PYRSUL:
SOFTEN:	ORGSUL:
FLUID:	SULFATE:
FREESWL:	

State: ND
County: WILLIAMS
TWP: 155 NS: N
RGE: 100 EW: W
section: 22
Q1: C Q2: D Q3:

Year: 1966
Source: 1
Author: GNRWY

Stratigraphic control
Top-E1: 2080
TK/Sec: 228.17
CoalOV: 59

Document 21

Cenozoic Project Geochemical Database Field Name Explanations Used in the Geographic-Geologic-Bibliographic Database

Geographic-Geologic-Bibliographic Data File (Part 1)

Field Name Explanations are used as per LeFever and Murphy (1983)

LOCALITY

The identification number for a particular location from which various types of data have been derived. More than one location number may refer to the same position, as in the case of a drill hole that encounters more than one lignite bed. Every sample taken from such a drill hole will receive a different locality number.

STATE

The postal abbreviation of the state in which the locality occurs.

COUNTY

The first ten letters of the county name. No abbreviations and with the spaces left in.

T (Township)

The township number in which the locality occurs.

NS (north/south)

The letter indicating whether the township lies north or south of the base line.

R (Range)

The range number in which the locality occurs.

EW (east/west)

The letter indicating whether the township lies east or west of the principal meridian.

SECTION

The section number in which the locality occurs.

Q1 (1st quarter)

The first letter in the ABCD quarter-section system.

Q2 (2nd quarter)

The second letter in the ABCD quarter-section system.

Q3 (3rd quarter)

The third letter in the ABCD quarter-section system.

Q4 (4th quarter)

The fourth letter in the ABCD quarter-section system.

FIELD

The coal field name, if one exists.

FM (Formation)

The abbreviation of the formation in which the locality occurs.

- TPAC - Paleocene undifferentiated
- TFU - Fort Union Formation or Group
- TTR - Tongue River Formation
- TSB - Sentinel Butte Formation
- TSBTR - Sentinel Butte/Tongue River
- TBC - Bullion Creek Formation
- TS - Slope Formation
- TC - Cannonball Formation
- TL - Ludlow Formation
- TLHC - Ludlow/Hell Creek
- TEC - Eocene undifferentiated
- TT - Tullock Formation
- TW - Wasatch Formation

SYSTEM

All entries set for the Tertiary System (TER).

SERIES

The geologic series to which the formation(s) belong. Paleocene = PAL;
Eocene = EOC.

DTYPE (Data type)

H - Drill hole; O - Outcrop; S - Single sample

ODS1 (other data sets, field 1)

A letter designation which indicates what types of data sets were derived from this locality.

- L - lithologic data
- C - coal chemistry data
- G - rock geochemistry data
- M - rock mineralogy data
- H - ground water data

ODS2 (other data sets, field 2)

See ODS1 for explanation.

ODS3 (other data sets, field 3)

See ODS1 for explanation.

ODS4 (other data sets, field 4)

See ODS1 for explanation.

ODS5 (other data sets, field 5)

See ODS1 for explanation.

YEAR

The year of the source publication.

SOURCE

The abbreviation methodology for an agency or institution and/or document type. The full source citation is made by combining the agency of organization with the document type, as in USGS PP, AAPG BULL, GSA MEM, or WYGA GB. For specific journals, only the single abbreviation (JSP) is shown.

Federal agencies –

USGS – United States Geological Survey
USBM – United States Bureau of Mines

State agencies (the state abbreviation followed by the agency abbreviation ,i.e., NDGS, MTGS) –

GS – Geological Survey
BM – Bureau of Mines
DM – Division of Mines

Organizations –

AAPG American Association of Petroleum Geologists
AAPGRM American Association of Petroleum Geologists, Rocky Mountain Section
WYGA Wyoming Geological Association
RMAG Rocky Mountain Association of Geologists
GSA Geological Society of America
SEPM Society of Economic Paleontologists and Mineralogists
SEPMRM Society of Economic Paleontologists and Mineralogists, Rocky Mountain Section.

Document types –

BULL Bulletin
CIRC Circular
MEM Memoir
JOUR Journal
GB Guidebook
PP Professional Paper
SP Special Paper/Special Publication
MAP Map
OFR Open-file Report
RI Report of investigation
MI Miscellaneous investigation
CR County reports
AN RPT Annual report
BI RPT Biennial report

Specific Journals –

JSP Journal of Sedimentary Petrology
SED Sedimentology
SG Sedimentary Geology
MG Mountain Geologist

Theses and Dissertations -

Theses from state institutions should be abbreviated with the state and institution acronym, as in UND or MTST, followed either by TH (for Master's) or DS (Ph.D). For other schools, the full (standard) acronym should be given, depending on name length, followed by TH or DS.

Industry source -

IND

Author

The following rules apply: Author's last name for theses and dissertations; the publication or volume number for agencies and organizations; and the first page number for journal articles.

LAT (Latitude)

The latitude was calculated by a computer program designed by R.D. LeFever. The value is calculated on the basis of the quarter-quarter subdivision. This value is not intended to be exact.

LONG (Longitude)

The longitude was calculated by a computer program designed by R.D. LeFever. The value is calculated on the basis of the quarter-quarter subdivision. This value is not intended to be exact.

X

The x-value of an X-Y coordinate system set up by R.D. LeFever. The origin of the system is approximately the southwest corner of North Dakota.

Y

The y-value of an X-Y coordinate system set up by R.D. LeFever. The origin of the system is approximately the southwest corner of North Dakota.

Document 21, continued

Lithologic Data File (Part II)

**Geochemical Field Name Explanations
Used in the Lithologic Database**

Locality

The reference number of the locality from which relevant data was derived. The geologic, geographic and bibliographic data associated with this locality number is located in the GEOLOGIC/GEOGRAPHIC/BIBLIOGRAPHIC data file. A Q&A® programming statement pulls the location and source data out of this file and inserts it into the fields to the right.

TSECT (thickness of section)

The total section thickness in feet x 10.

TOPELEV (top elevation)

The elevation (in feet) of the section top.

NCG (number of conglomerate beds)

The number of conglomerate beds in the section.

TCG (thickness of conglomerate)

The total bed thickness (in feet x 10) of the conglomerates in the section.

NSS (number of sandstone beds)

The number of sandstone beds in the section.

TSS (thickness of sandstone)

The total bed thickness (in feet x 10) of the sandstones in the section.

NSH (number of siltstone/shale beds)

The number of siltstone/shale beds in the section.

TSH (thickness of siltstone/shale)

The total bed thickness (in feet x 10) of the siltstones/shales in the section.

NLS (number of limestone beds)

The number of limestone beds in the section.

TLS (thickness of limestone)

The total bed thickness (in feet x 10) of the limestones in the section,

NCL (number of coal beds)

The number of coal beds in the section.

TCL (thickness of coal)

The total bed thickness (in feet x 10) of the coals in the section.

NCK (number of clinker beds)

The number of clinker beds in the section.

TCK (thickness of clinker)

The total bed thickness (in feet x 10) of the clinkers in the section.

COALNAME

The name of the coal bed used at the time of the source.

COALOV (Overburden)

The thickness of rock above the indicated coal (in feet x 10).

COALRES (coal reserves)

Coal reserves in millions of tons x 100.

CRTYPE (coal reserve type)

Type of coal reserve (see USGS classification).

URRES (uranium reserves)

Uranium reserves in millions of tons x 100.

URTYPE (uranium reserve type)

Type of uranium reserve (see USGS classification).

MEAN (mean direction in azimuth degrees)

The mean value (in azimuth degrees) of paleocurrent directional data collected at this locality (if any).

SD (standard deviation)

The standard deviation of the paleocurrent directional data.

DDTYPE (directional data type)

A code to indicate what type of directional data was used. The codes are: XB - cross-bedded; RM - ripple marks; CH - channeling; CO - combination; OT - other.

Document 21, continued

Coal Chemistry Data File (Part III)

**Geochemical Field Name Explanations
Used in the Coal Chemistry Database**

LOCALITY

The reference number of the locality from which the data was derived. The geologic, geographic and bibliographic data associated with this locality number is located in the GEOLOGIC/GEOGRAPHIC/BIBLIOGRAPHIC data file. A Q&A® programming statement pulls the location and source data out of this file and inserts it into the fields to the right (see Document 20).

RANK

LG - Lignite; SB - Subbituminous; BT - Bituminous

STYPE (Sample type)

C - Channel; R - Run of mine; D - Drill core; O - other.

ATYPE (Analysis type)

0 - as received
1 - air dried
2 - moisture free
3 - moisture and ash free
4 - other

VALUES

The analysis values represent:
0 - single sample
1 - average of more than one sample
2 - other

TRACE

A yes/no field indicating the presence of trace elements in the analysis.

ODATA (other data)

A yes/no field indicating whether there is additional data available in the original source.

GRIND

The Hardgrove grindability index.

BTU

The BTU value of the sample.

DEFORM

Ash deformation temperature in degrees fahrenheit.

SOFTEN

Ash softening temperature in degrees fahrenheit.

FLUID

Ash fluid temperature in degrees fahrenheit.

FREESWL (Free-swelling index)

The value is the index x 10.

MOISTURE

The moisture content in percent.

VOLATILE

The amount of volatile matter in percent.

FCARBON (Fixed carbon)

The amount of fixed carbon in percent.

ASH

The ash content in percent x 10.

H

The hydrogen content in percent x 10.

CARBON

The total carbon content in percent x 10.

OXYGEN

The oxygen content in percent x 10.

NITROGEN

The nitrogen content in percent x 10.

S

The sulfur content in percent x 10.

PYRSUL

The content of pyritic sulfur in percent x 10.

ORGSUL

The content of organic sulfur in percent x 10.

SULFATE

The sulfate content in percent x 10.

STRATIGRAPHIC CONTROL

This information is derived from the LITHOLOGIC data file and is entered in this data file through a Q&A® programming statement.

Top-E1	The surface elevation at the top of the stratigraphic section (outcrop or drill hole).
TK/Sec	The thickness (in feet x 10) of the stratigraphic section corresponding to this locality number.
Coal10V	The amount of overburden on the specified coal bed.

Appendix V

Geochemical Database Design A Summary of Alternative Approaches to Coal Chemistry Database Management

Document 22

Example of a Q&A® Coal Chemistry Database

M-number: Ref:

Prox. Analysis	As det.	As recd.	MoistFree	Moist/ashFree	
%Moisture	:	:	:	:	Rank:
%Volatile	:	:	:	:	Stype:
%FCarbon	:	:	:	:	Values:
%Ash	:	:	:	:	
%Hydrogen	:	:	:	:	Date sampled
%Carbon	:	:	:	:	:
%Nitrogen	:	:	:	:	Date received
%Sulfur	:	:	:	:	:
%Oxygen	:	:	:	:	Date of report
Btu	:	:	:	:	:

%As rec. H: %Sulfate: DefoTemp: Air dry loss:

%As rec. O: %Pyrsulf: SoftTemp:-

Grind: %Orgsulf: Hemisph:

 Red/Ox: FluidTemp:

TrElements:

TestType: Modified: :

Screen Page 2

M-number: Ref:

State:		-----EERC Specific-----
County:		GF #:
Field:		Lab #:
Bed name:		Run #:
Unit Number:		Sample Desc:
Quad:		Submitter:

Formation:

El/ft: El/m:

Tk/ft: Tk/m:

Overburden/ft:

Overburden/m:

Document 23

Coal Analysis Report Derived from Q&A®
Coal Chemistry and *MNOS Databases

Example M2075 - Bed 1

Analysis data for **Bed 1 of M2075** as provided by Great Northern Railway Co.
Report no. 27. This sample is from the Avoca Lignite Field in Williams
County, ND.

	As Det. (%)	As Recd. (%)	Moist. Free (%)	Moist/Ash Free (%)
Proximate Analysis				
Moisture		40.57		
Volatile Matter		25.66	43.17	
Fixed Carbon		26.53	44.64	
Ash		7.24	12.19	
Ultimate Analysis				
Hydrogen				
Carbon				
Nitrogen				
Sulfur		1.38	2.33	
Oxygen				
Ash		7.24	12.19	
Heating value (Btu/lb)				
		6533.0	10993.0	

As received hydrogen not including hydrogen from moisture: %
As received oxygen not including oxygen from moisture: %
Air dry loss: %

Sulfur Forms in percent:	Ash fusion temperatures (degrees F):
Sulfate:	Initial deformation:
Pyritic:	Softening: 2360
Organic:	Hemispherical:
	Fluid:

Location Information

M2075 lies in the C sec. 25, T. 155 N., R. 100 W., of the Williston East
quadrangle. This bed has a thickness of 6.60 ft (2.01 m), and its base is
at an elevation of 1975.58 ft.

Stratigraphic Information

Bed 1 is within the Sentinel Butte Formation of ND.

*More detailed stratigraphic information is available in association with M2075 of the *MNOS and/or
*UNITS data files.

UND EERC-Specifics

GF number :	Date sampled :
Lab number:	Date received :
Run number:	Date of report: 1953
Submitter :	
Sample description:	
Comments:	

**Coal Analysis Report Derived from Q&A®
Coal Chemistry and *MNOS Databases**

Example M2075 – Bed 2

Analysis data for **Bed 2 of M2075** as provided by Great Northern Railway Co. Report no. 27. This sample is from the Avoca Lignite Field in Williams County, ND.

	As Det. (%)	As Recd. (%)	Moist. Free (%)	Moist/Ash Free (%)
Proximate Analysis				
Moisture		38.94		
Volatile Matter		25.86	42.35	
Fixed Carbon		27.96	45.80	
Ash		7.24	11.85	
Ultimate Analysis				
Hydrogen				
Carbon				
Nitrogen				
Sulfur		0.64	1.05	
Oxygen				
Ash		7.24	11.85	
Heating value (Btu/lb)				
		6700.0	10973.0	

As received hydrogen not including hydrogen from moisture: %

As received oxygen not including oxygen from moisture: %

Air dry loss: %

Sulfur Forms in percent:

Sulfate:

Pyritic:

Organic:

Ash fusion temperatures (degrees F):

Initial deformation:

Softening: 2065

Hemispherical:

Fluid:

Location Information

M2075 lies in the C sec. 25, T. 155 N., R. 100 W., of the Williston East quadrangle. This bed has a thickness of 4.83 ft (1.47 m), and its base is at an elevation of 1955.00 ft.

Stratigraphic Information

Bed 2 is within the Sentinel Butte Formation of ND.

*More detailed stratigraphic information is available in association with M2075 of the *MNOS and/or

*UNITS data files.

UND EERC-Specifics

GF number :

Lab number:

Run number:

Submitter :

Sample description:

Comments:

Date sampled :

Date received :

Date of report: 1953

**Coal Analysis Report Derived from Q&A®
Coal Chemistry and *MNOS Databases**

Example M2075 – Bed 3

Analysis data for **Bed 3 of M2075** as provided by Great Northern Railway Co. Report no. 27. This sample is from the Avoca Lignite Field in Williams County, ND.

	As Det. (%)	As Recd. (%)	Moist. Free (%)	Moist/Ash Free (%)
Proximate Analysis				
Moisture		40.50		
Volatile Matter		24.60	41.40	
Fixed Carbon		28.70	48.30	
Ash		6.10	10.20	
Ultimate Analysis				
Hydrogen				
Carbon				
Nitrogen				
Sulfur		0.63	1.06	
Oxygen				
Ash		6.10	10.20	
Heating value (Btu/lb)				
		6581.0	11066.0	

As received hydrogen not including hydrogen from moisture: %

As received oxygen not including oxygen from moisture: %

Air dry loss: %

Sulfur Forms in percent:

Sulfate:

Pyritic:

Organic:

Ash fusion temperatures (degrees F):

Initial deformation:

Softening: 2215

Hemispherical:

Fluid:

Location Information

M2075 lies in the C sec. 25, T. 155 N., R. 100 W., of the Williston East quadrangle. This bed has a thickness of 9.17 ft (2.80 m), and its base is at an elevation of 1880.42 ft.

Stratigraphic Information

Bed 3 is within the Sentinel Butte Formation of ND.

*More detailed stratigraphic information is available in association with M2075 of the *MNOS and/or *UNITS data files.

UND EERC-Specifics

GF number :

Lab number:

Run number:

Submitter :

Sample description:

Comments:

Date sampled :

Date received :

Date of report: 1953

Coal Analysis Report Derived from Q&A®
Coal Chemistry and *MNOS Databases

Example M2075 - Bed 4

Analysis data for Bed 4 of M2075 as provided by Great Northern Railway Co.
Report no. 27. This sample is from the Avoca Lignite Field in Williams
County, ND.

	As Det. (%)	As Recd. (%)	Moist. Free (%)	Moist/Ash Free (%)
Proximate Analysis				
Moisture		38.38		
Volatile Matter		22.55	36.60	
Fixed Carbon		25.32	41.18	
Ash		13.75	22.32	
Ultimate Analysis				
Hydrogen				
Carbon				
Nitrogen				
Sulfur		1.05	1.71	
Oxygen				
Ash		13.75	22.32	
Heating value (Btu/lb)				
		5925.0	9616.0	

As received hydrogen not including hydrogen from moisture: %
As received oxygen not including oxygen from moisture: %
Air dry loss: %

Sulfur Forms in percent:	Ash fusion temperatures (degrees F):
Sulfate:	Initial deformation:
Pyritic:	Softening: 2145
Organic:	Hemispherical:
	Fluid:

Location Information

M2075 lies in the C sec. 25, T. 155 N., R. 100 W., of the Williston East
quadrangle. This bed has a thickness of 11.00 ft (3.35 m), and its base is
at an elevation of 1829.67 ft.

Stratigraphic Information

Bed 4 is within the Sentinel Butte Formation of ND.

*More detailed stratigraphic information is available in association with M2075 of the *MNOS and/or *UNITS data
files.

UND EERC-Specifics

GF number :	Date sampled :
Lab number:	Date received :
Run number:	Date of report: 1953
Submitter :	
Sample description:	
Comments:	

Document 24

Coal Analysis Report Without Geographic Reference Data

An Example of a Coal Analysis Report Generated at EERC
(with minor cosmetic changes for this report)

GF NUMBER: 92-0196

LAB NUMBER: 5129

DATE SAMPLED : 1992/02/21

RUN NUMBER:

DATE RECEIVED : 1992/02/21

DATE OF REPORT: 1992/02/27

SAMPLE DESCRIPTION: (Blue) Mexican coal

SUBMITTER: GUNDERSON

Air dry loss: 0.32%

	As Det. (%)	As Recd. Free (%)	Moist. Free (%)	Moist/Ash Free (%)
Proximate Analysis				
Moisture	0.98	1.30		
Volatile Matter	21.56	21.49	21.78	32.80
Fixed Carbon	44.18	44.03	44.62	67.19
Ash	33.27	33.16	33.60	

	As Det. (%)	As Recd. Free (%)	Moist. Free (%)	Moist/Ash Free (%)
Ultimate Analysis				
Hydrogen	3.72	3.74	3.64	5.49
Carbon	57.68	57.49	58.25	87.72
Nitrogen	1.06	1.05	1.07	1.61
Sulfur	1.30	1.03	1.31	1.97
Oxygen	2.96	3.24	2.12	3.19
Ash	33.27	33.16	33.60	

Heating value (Btu/lb)

BTU	10096.0	10063.0	10195.0	15355.0
CALC. CALORIFIC VALUE	10182.0	10149.0		

As received hydrogen not including hydrogen from moisture: 3.59%
As received oxygen not including oxygen from moisture: 2.09%

Sulfur Forms in percent:

Sulfate:
Pyritic:
Organic:

Ash fusion temperatures (degrees F):

Initial deformation:
Softening:
Hemispherical:
Fluid:

Comments:

Document 25

Stratigraphic Data (*UNITS Database) for Coal Analysis Report

Example of drill hole section M2075 Data from the *UNITS Database used in the Coal Chemistry Report (Document 23)

Units (in feet) Summed from Top with Elevations: M2075

MMRRI Sect. No.	Sect. Unit No.	Unit THICK ft	Bed Name	Feet From Top of Section	Elevation of Units (ft)	Original Lithologic Description
M2075	000	0.000		0.000	2051.000	Top of section. Great Northern Railway Co. hole 2
M2075	001	32.000		32.000	2019.000	"Sand, gravel, and glacial clay"
M2075	002	2.000		34.000	2017.000	"Lignite, woody, and petrified wood"
M2075	003	24.250		58.250	1992.750	"Gray clay and gray shale"
M2075	004	2.917		61.167	1989.833	"Lignite, salvage vein"
M2075	005	7.667		68.834	1982.166	"Light gray clay"
M2075	006	6.583	Bed 1-GNRwy	75.417	1975.583	"Lignite" [Bed 1]
M2075	007	15.750		91.167	1959.833	"Gray silty clay and traces of lignite"
M2075	008	4.833	Bed 2-GNRwy	96.000	1955.000	"Lignite" [Bed 2]
M2075	009	30.417		126.417	1924.583	"Green-gray silty clay"
M2075	010	1.250		127.667	1923.333	"Lignite, woody"
M2075	011	33.750		161.417	1889.583	"Green-gray silty clay"
M2075	012	9.167	Bed 3-GNRwy	170.584	1880.416	"Lignite" [Bed 3]
M2075	013	38.750		209.334	1841.666	"Green-gray silty clay and lignite stringers"
M2075	014	1.000		210.334	1840.666	"Lignite and carbonaceous clay"
M2075	015	11.000	Bed 4-GNRwy	221.334	1829.666	"Lignite" [Bed 4]
M2075	016	3.666		225.000	1826.000	"Green-gray silty clay"
M2075	017	0.000		225.000	1826.000	Bottom of section.

(BLWtpELEV.DH-WBUNIT.DTF) 7/14/92, 8:29 am, p. 1

Document 26

Geographic Data (*MNOS Database) for Coal Analysis Report

Example of drill hole section M2075 Data from the *UNITS Database used in the Coal Chemistry Report (Document 23)

WILLISTON BASIN M-NUMBER LOCALITY FORM

Joseph H. Hartman, UND-EERC-MMRI

data entered on: 1991/01/15; form printed on: 1992/07/14

M2075

LOG TYPE: DH

REFERENCE : Great Northern Railway Co. Report no. 27, p. 53
 REFERENCE BOSS : ()
 OBSERVATION BY : ()
 INTERPRETED BY : ()
 REFERENCE # :
 ORIGINAL FIELD# : Hole 2
 INSTITUTION # :
 DRILL LOG TYPES :
 FOSSIL L-numbers : ()

ADDITIONAL # :
 LOCALITY NAME :
 PANEL DATA : AREA CROSS SEC COLUMN
 NCRDS RELATED : NCRDS: SUMc: HEADc: LOGc:

M-number LOCATION DATA

GENERAL LOCATION : USA, ND, William County STUDY AREA: WB-FTU region, Avcoas Lignite Field field area
 QUADRANGLE DATA : Williston East Quad., 1976, 7.5 series, 10 foot contour interval (map location: 48103, B5)
 LEGAL LOCATION : C sec. 25, T. 155 N., R. 100 W. (CODES- sec: ; TWP: ; RGE: ; X: ; BLM:)
 FROM SECTION LINE : feet , feet ; meters , meters
 ILLUSTRATIONS :
 SITE DESCRIPTION : "C 25 155N 100W." "El. 2051."

PLOTTED (Y/N)- 24k: Y 100k: Y

STRATIGRAPHIC DATA

Litho- and Chronostratigraphy of Section (1 to 4 = bottom to top)

SERIES4: QUA	FORMATION: glacial sediment	THICKNESS: 32.000 feet; 9.754 meters	C4:
SERIES3: PAL	FORMATION: Sentinel Butte	THICKNESS: 193.000 feet; 58.827 meters	C3:
SERIES2:	FORMATION:	THICKNESS: feet; meters	C2:
SERIES1:	FORMATION:	THICKNESS: feet; meters	C1:

Section Thickness and Elevations

SECTION THICKNESS : 225.000 feet; 68.581 meters
 ELEV TOP OF SECTION : 2051.000 feet; 625.152 meters ELEVATION +/- : feet; meters
 ELEV BASE OF SECTION : 1826.000 feet; 556.572 meters INTERPRETED BY : GIVEN

Bed Nomenclature and Data

PRIMARY FORMATION : Sentinel Butte LITHIC COLLNS :
 ORIGINAL BED NAME : UNIT # : BED Code:
 REVISED BED NAME :
 NAMED BEDS IN SECTION : Bed 1, Bed 2, Bed 3, Bed 4

Stratigraphic Correlation and Description

Labeled lignite Beds 1 to 4 from top to bottom.

GENERAL M-number COMMENTS

APPENDIX VI

*MNOS Bibliographic References

Document 27

Bibliography of Primary Coal Resource Data

North Dakota Bibliography

- Anna, L.O., 1980, Ground-water data for Billings, Golden Valley and Slope Counties, North Dakota: North Dakota Geological Survey, Bulletin 76, part II, 241 p., 1 pl.
- Archibald, J.D., 1981 [1982], A study of mammalia and geology across the Cretaceous-Tertiary boundary in Garfield County, Montana: Berkeley, University of California Press, 286 p.
- Armstrong, C.A., 1967, Geology and ground water resources, Williams County, North Dakota: North Dakota Geological Survey, Bulletin 48, part 2, 132 p.
- Banet, A.C., Jr., 1980, Coal geology and resource calculations of the south Belfield area, Billings and Stark Counties, North Dakota: U.S. Geological Survey, Open-file Report 80-870, 18 p., 11 pls.
- Bauer, C.M., see Hares, USGS Field Record Library accession numbers, 1911 unpublished field notes for Golden Valley County utilized in part by Hares (1928).
- Beekly, A.L., 1912, The Culbertson lignite field, Valley County, Montana: United States Geological Survey, Bulletin 471-D, p. 319-358, pl. XXVI-XXVII.
- Belt, E.S., written communication, 1986, unpublished measured sections in Golden Valley and Slope Counties, North Dakota.
- Belt, E.S., Flores, R.M., Warwick, P.D., Conway, K.M., Johnson, K.R., and Waskowitz, R.S., 1984, Relationship of fluviodeltaic facies to coal deposition in the lower Fort Union Formation (Paleocene), south-western North Dakota, in Collinson, J.D., and Lewin, J., eds., Modern and ancient fluvial systems: International Association of Sedimentologists, Special Publication 6, p. 177-195.
- Bluemle, J.P., 1971, Geology of McLean County, North Dakota: North Dakota Geological Survey, Bulletin 60, part I, 65 p., 3 pls.
- Carlson, C.G., 1973, Geology of Mercer and Oliver Counties, North Dakota: North Dakota Geological Survey, Bulletin 56, part I, 72 p., 4 pls.

- Carlson, C.G., 1983, Geology of Billings, Golden Valley, and Slope Counties, North Dakota: North Dakota Geological Survey, Bulletin 76, part I, 40 p., 5 pls.
- Clark, M.B., 1966, The stratigraphy of the Sperati Point Quadrangle, McKenzie County, North Dakota [M.A. thesis]: Grand Forks, University of North Dakota, 108 p., 4 pls.
- Collier, A.J., 1918, The Nesson anticline, Williams County, North Dakota: United States Geological Survey, Bulletin 691-G, p. 211-217, pl. XXVI.
- Conway, K.M., 1982, Sedimentology of fluvial facies in the upper Ludlow and lower Tongue River Members of the Fort Union Formation (Paleocene), southwestern North Dakota [B.A. honors thesis]: Amherst, Amherst College, 120 p., plus "long sections."
- Cook, S.M., and Spencer, J.M., 1979, Geophysical and lithologic logs for 1978 coal drilling in Mountrail, Renville, Ward, and Williams Counties, North Dakota: U. S. Geological Survey, Open-file Report 79-912, 124 p.
- Crawford, J.W., 1967, Stratigraphy and sedimentology of the Tongue River Formation (Paleocene), southeast Golden Valley County, North Dakota [M.S. thesis]: Grand Forks, University of North Dakota, 73 p., 3 pls.
- Croft, M.G., 1985, Ground-water data for McKenzie County, North Dakota: North Dakota Geological Survey, Bulletin 80, part 2, 455 p.
- Delimata, J.J., 1969, Fort Union (Paleocene) mollusks from southern Golden Valley and southeastern Billings Counties, North Dakota [M.S. thesis]: Grand Forks, University of North Dakota, 73 p., 6 pls.
- Denson, N.M., Bachman, G.O., and Zeller, H.D., 1959, Uranium-bearing lignite in northwestern South Dakota and adjacent states: U.S. Geological Survey, Bulletin 1055-B, p. 11-57, 16 pls.
- Dove, L.P., and Eaton, H.N., 1925, Williams and Mountrail Counties, *in* Leonard, A.G., Babcock, E.J., and Dove, L.P., North Dakota Geological Survey, Bulletin 4, p. 153-165, pl. XIV-XV.
- Fisher, S.P., Jr., 1953, Geology of west central McKenzie County, North Dakota: North Dakota Geological Survey, Report of Investigations no. 11, 2 sheets.
- Fisher, S.P., Jr., 1954, Structural geology of the Skaar-Trotters area, McKenzie and Golden Valley Counties, North Dakota: North Dakota Geological Survey, Report of Investigations no. 15, 1 sheet.
- Flores, R.M., and Lepp, C.L., 1983, Environmental-stratigraphic cross sections of the Cretaceous Fox Hills sandstone and Hell Creek Formation and Paleocene Fort Union Formation, Richland and Roosevelt Counties, Montana: U.S. Geological Survey Miscellaneous Field Studies Map, MF-1554, 1 sheet.

- Freers, T.F., 1970, Geology and ground water resources, Williams County, North Dakota: North Dakota State Geological Survey, Bulletin 48, part 1, 55 p.
- Great Northern Railway Company Report, 1955, Lignite drilling program, Williston Basin, North Dakota and Montana, 1953-1955: Great Northern Railway Company, Mineral Research and Development Department, Report no. 1, 4 p., pls. A-P, plus appendixes.
- Great Northern Railway Company, 1966, The Avoca lignite deposit, Williams County, North Dakota: Great Northern Railway Company, Mineral Research and Development Department, Report no. 27, 65 p., XI pls.
- Gregory Drilling, 1984, 1988, and 1990, unpublished descriptive drilling logs for water wells in Fallon County, Montana: Gregory Drilling, Inc., Dickinson, North Dakota.
- Hanson, 1955, Geology of the Elkhorn Ranch area, Billings and Golden Valley Counties, North Dakota: North Dakota Geological Survey, Report of Investigations no. 18, 1 sheet.
- Hares, C.J., 1911 unpublished field notes for Golden Valley County utilized in part by Hares (1928).
- Hares, C.J., 1928, Geology and lignite resources of the Marmarth field, southwestern North Dakota: U.S. Geological Survey, Bulletin 775, 110 p.
- Harksen, J.C., 1978, Geophysical and lithologic logs for 1977 coal drilling in Wibaux County, Montana, and Golden Valley County, North Dakota: U.S. Geological Survey, Open-file Report 78-251, 185 p.
- Hartman, J.H., 1984, Systematics, biostratigraphy, and biogeography of latest Cretaceous and early Tertiary Viviparidae (Mollusca, Gastropoda) of southern Saskatchewan, western North Dakota, eastern Montana, and northern Wyoming [Ph.D. Thesis]: Minneapolis, University of Minnesota, 928 p., 19 pls. [Dissertation Abstracts International, v. 45, no. 3].
- Hartman, J.H., 1986, 1988, 1990, and 1991 unpublished field notes for ongoing research in Billings, Golden Valley, and Williams Counties, North Dakota.
- Herald, F.A., 1913, The Williston lignite field, Williams County, North Dakota: U.S. Geological Survey, Bulletin 531-F, p. 91-157, pls. IX-X.
- Hayden, F.V., 1859, Geological sketch of the estuary and fresh water deposit of the Bad Lands of the Judith, with some remarks upon the surrounding formations: American Philosophical Society, Transactions, n.s., v. 11, p. 123-138, pl. 8.
- Hayden, F.V., 1862, On the geology and natural history of the Upper Missouri: American Philosophical Society, Transactions, v. 12, n.s., p. 1-218, map.

- Jacob, A.F., 1973, Depositional environments of Paleocene Tongue River Formation, western North Dakota: American Association of Petroleum Geologists, Bulletin 57, p. 1038-1052.
- Jacob, A.F., 1976, Geology of the upper part of the Fort Union Group (Paleocene), Williston Basin, with reference to uranium: North Dakota Geological Survey, Report of Investigation no. 58, 49 p.
- Johnson, R.P., 1973, Depositional environments of the upper part of the Sentinel Butte Formation, southeastern McKenzie County, North Dakota [M.S. thesis]: Grand Forks, University of North Dakota, 63 p.
- Kihm, A.J., 1990 unpublished field notes for ongoing research in Williams County, North Dakota.
- Kroeger, T.J., 1988, unpublished field notes for ongoing research in Slope County, North Dakota.
- LeFever, R.D., and Murphy, E.C., 1983, Final Report: Mining Resources and potential problems associated with mining of Cenozoic rocks of the Williston and Powder River Basins, northern Great Plains: Washington, D.C., U.S. Department of the Interior, Office of Surface Mining, Division of Technical Services and Research, 170 p.
- Leonard, A.G., 1904, Topographic features and geological formations of North Dakota: North Dakota Geological Survey, Third Biennial Report, p. 129-177.
- Leonard, A.G., 1906, The North Dakota-Montana lignite area: U.S. Geological Survey, Bulletin 285, p. 316-330.
- Leonard, A.G., 1908, Geology of southwestern North Dakota, with special reference to the coal: North Dakota Geological Survey, Fifth Biennial Report, p. 27-114, pls. I-XIX.
- Leonard, A.G., 1911, The Cretaceous and Tertiary Formations of western North Dakota and eastern Montana: Journal of Geology, v. 19, p. 507-547.
- Leonard, A.G. 1925, Billings and Golden Valley Counties, in Leonard, A.G., Babcock, E.J., and Dove, L.P., North Dakota Geological Survey, Bulletin 4, p. 34-58, pl. IV-VI.
- Leonard, A.G., and Smith, C.D., 1909, The Sentinel Butte lignite field, North Dakota and Montana: U.S. Geological Survey, Bulletin 341-A, p. 15-35.
- Meldhal, E.G., 1956, The geology of the Grassy Butte area, McKenzie County, North Dakota [M.S. thesis]: Grand Forks, University of North Dakota, 42 p., 1 pl.
- Meldhal, E.G., 1956, The geology of the Grassy Butte area, McKenzie County, North Dakota: North Dakota Geological Survey, Report of Investigations no. 26, 1 sheet.

- Menge, M.L., 1977, Preliminary report on the coal resources of the Dickinson area, Billings, Dunn, and Stark Counties, North Dakota: U.S. Geological Survey, Open-file Report 77-482, 11 p., 13 pls.
- Menge, M.L., 1980, Geophysical and lithologic logs for 1979 coal drilling, Three River area, Stark, Billings, and Dunn Counties, North Dakota: U.S. Geological Survey, Open-file Report 80-860, 288 p.
- Moore, W.L., 1976, The stratigraphy and environments of deposition of the Cretaceous Hell Creek Formation (reconnaissance) and the Paleocene Ludlow Formation (detailed), southwestern North Dakota: North Dakota Geological Survey, Report of Investigations no. 56, 40 p.
- Nesemeier, B.D., 1981, Stratigraphy and sedimentology of the Sentinel Butte Formation (Paleocene) near Lost Bridge, Dunn County, west-central North Dakota [M.S. thesis]: Grand Forks, University of North Dakota, 67 p., 1 pl.
- Nevin, C., 1946, The Keene dome, northeast McKenzie County, North Dakota: North Dakota Geological Survey, Bulletin 21, part I, p. 1-10, pl. 1.
- North Dakota Geological Survey, unpublished relevant oil and gas drill hole records.
- Peck, W.D., 1989 and 1990 unpublished field notes for the Lake Jessie area, Williams County, North Dakota, as part of ongoing studies for a master's thesis at the University of North Dakota.
- Perkins, R.K., 1987, Depositional environments of a portion of the Bullion Creek Formation (Paleocene), western Billings County, North Dakota [M.S. thesis]: Grand Forks, University of North Dakota, 244 p.
- Pipiringos, G.N., Chisholm, W.A., and Kepferle, R.C., 1965, Geology and uranium deposits in the Cave Hills area, Harding County, South Dakota: U.S. Geological Survey, Professional Paper 476-A, 64 p.
- Robertson, E.B., 1975, Pollen and spores as stratigraphic indices to the North Dakota Paleocene [Ph.D. dissertation]: Minneapolis, University of Minnesota, 192 p., 3 pls.
- Royse, C.F., Jr., 1967, A stratigraphic and sedimentologic analysis of the Tongue River and Sentinel Butte Formations (Paleocene), western North Dakota [Ph.D. dissertation]: Grand Forks, University of North Dakota, 312 p., 1 pl.
- Sholes, M.A., 1988, Coal resources of the Baker and Wibaux 30x60-minute quadrangles, eastern Montana and adjacent North Dakota: Montana Bureau of Mines and Geology Geologic Map Series No. 48 (map scale 1:100,000).

- Sholes, M.A., Vuke-Foster, S.M., and Derkey, P.D., 1989, Coal stratigraphy and correlation in the Glendive 30x60-minute quadrangle, eastern Montana and adjacent North Dakota: Montana Bureau of Mines and Geology, Geologic Map 49, 9 p., 4 sheets.
- Spencer, J.M., 1978a, Lignite geology of southeast Williams County, North Dakota: U.S. Geological Survey, Open-file Report 78-168, 13 p.
- Spencer, J.M., 1978b, Geophysical and lithologic logs for 1977 coal drilling in McKenzie County, North Dakota: U.S. Geological Survey, Open-file Report 78-451, 161 p.
- Spencer, J.M., 1980, Geophysical and lithologic logs for 1979 drilling in Williams County, North Dakota: U.S. Geological Survey, Open-file Report 80-646, 114 p.
- Spencer, J.M., 1981a, Lignite geology of the Keene area, McKenzie County, North Dakota: U. S. Geological Survey, Open-file Report 81-602, 8 p.
- Spencer, J.M., 1981b, Geologic map and lignite resources of the Cussicks Spring Quadrangle, Williams County, North Dakota: U. S. Geological Survey, Coal Investigations Map C-89, 2 sheets (map scale 1:24000).
- Steiner, M.A., 1978, Petrology of sandstones from the Bullion Creek and Sentinel Butte Formations (Paleocene), Little Missouri badlands, North Dakota [M.S. thesis]: Grand Forks, University of North Dakota, 153 p.
- Stevenson, R.E., 1956, Areal geology of the Ludlow quadrangle: South Dakota State Geological Survey (map scale 1:62,500).
- U.S. Geological Survey, 1976a, Preliminary report of coals drillhole data and chemical analyses of coal beds in Campbell and Sheridan Counties, Wyoming: Custer, Prairie, and Garfield Counties, Montana: and Mercer County, North Dakota: U.S. Geological Survey, Open-file Report 76-319, 352 p.
- U.S. Geological Survey, 1976b, Preliminary report on 1975 drilling of lignites in western North Dakota: Adams, Bowman, Dunn, Hettinger, McLean, Mercer, Oliver, Slope, and Williams Counties: U.S. Geological Survey, Open-file Report 76-869, 144 p.
- U.S. Geological Survey, 1978, Lignite drilling during 1977 in western North Dakota: Adams, Billings, Bowman, Dunn, Grant, Golden Valley, Hettinger, Mercer, Oliver, Slope, Stark, and Williams Counties: U.S. Geological Survey, Open-file Report 78-888, 541 p.
- U.S. Geological Survey, 1979, Lignite drilling during 1978 in western North Dakota: Adams, Billings, Bowman, Burke, Golden Valley, Hettinger, McKenzie, McLean, and Slope Counties: U.S. Geological Survey, Open-file Report 79-1051, 519 p.

- U.S. Geological Survey, 1980, Lignite drilling during 1979 in Ward, Mountrail, and Divide Counties, western North Dakota: U.S. Geological Survey, Open-file Report 80-867, 392 p.
- U.S. Geological Survey, 1981, Coal drilling during 1979 in Williams County, North Dakota, and in Beaverhead, Big Horn, Dawson, Fallon, Garfield, McCone, Musselshell, Powder River, Prairie, Roosevelt, Rosebud, and Wibaux Counties, Montana: U.S. Geological Survey, Open-file Report 81-314 , 613 p.
- Van Alstine, J.B., 1974, Paleontology of brackish-water faunas in two tongues of the Cannonball Formation (Paleocene, Danian), Slope and Golden Valley Counties, southwestern North Dakota [Master's Thesis]: Grand Forks, University of North Dakota, 101 p.
- Vuke-Foster, S.M., Colton, R.B., Stickney, M.C., Wilde, E.M., Robocker, J.E., and Christensen, K.C., 1986, Geology of the Baker and Wibaux 30x60-minute quadrangles, eastern Montana and adjacent North Dakota: Montana Bureau of Mines and Geology, Geologic Map 41, 1 sheet.
- Wallick, B.P., 1984, Sedimentology of the Bullion Creek and Sentinel Butte Formations (Paleocene) in a part of southern McKenzie County, North Dakota [Master's thesis]: Grand Forks, University of North Dakota, 245 p., 3 pl.
- Warwick, P.D., 1982 unpublished field notes for Billings and Golden Valley Counties utilized in part in Warwick (1982).
- Warwick, P.D., 1982, The geology of some lignite-bearing fluvial deposits (Paleocene), southwestern North Dakota [Master's thesis]: Raleigh, North Carolina State University, 98 p.
- Waskowitz, R.S., 1982, The sedimentology of the lower Paleocene Ludlow Member of the Fort Union Formation, southwestern North Dakota [Senior thesis]: Amherst, Amherst College, 107 p.
- Wilder, F.A., 1903, The lignite deposits of Williams County and vicinity: North Dakota Geological Survey, Second Biennial Report, v. 1, no. 1, p. 56-60.
- Wilder, F.A., 1904a, The lignite on the Missouri, Heart and Cannon Ball Rivers and its relation to irrigation: North Dakota Geological Survey, Third Biennial Report, p. 9-40.
- Wilder, F.A., 1904b, The Laramie and Fort Union beds in North Dakota: Journal of Geology, v. 12, no. 4, p. 290-293.

Montana Bibliography

- Banet, A.C., 1979, Preliminary geologic investigation of the West Glendive lignite deposits, Dawson County, Montana: U.S. Geological Survey, Open-file report 79-275, 11 p.
- Christensen, K.C., 1984, The stratigraphy and petrography of a light-colored siliceous horizon within the Fort Union Formation (Paleocene), southeastern Montana [M.S. thesis]: Butte, Montana College of Mineral Science and Technology, 183 p.
- Hance, J.H., 1912, The Glendive lignite field, Dawson County, Montana: U.S. Geological Survey, Bulletin 471-D, p. 271-283.
- Lewis, R.C., and Harksen, J.C., 1980, Coal geology of the Wibaux-Beach area, Wibaux County, Montana, and Golden Valley County, North Dakota: U.S. Geological Survey, Open-file Report 80-166, 37 p.
- Mathews, J.E., 1989a, Coal stratigraphy and correlation in the Sidney 30x60-minute quadrangle, eastern Montana and adjacent North Dakota [Index map, cross section, and fence diagram], with a descriptive text, J.E. Mathews and E.M. Wilde: Montana Bureau of Mines and Geology, Geologic Map No. 50-A (map scale 1:100,000).
- Mathews, J.E., 1989c, Coal stratigraphy and correlation in the Sidney 30x60-minute quadrangle, eastern Montana and adjacent North Dakota [Coal and clinker outcrop, structure contour, coal isopach, and interburden isopach maps of the Budka, Lane, and Carroll intervals], with a descriptive text, J.E. Mathews and E.M. Wilde: Montana Bureau of Mines and Geology, Geologic Map No. 50-C (map scale 1:100,000).
- Mathews, J.E., 1989b, Coal stratigraphy and correlation in the Sidney 30x60-minute quadrangle, eastern Montana and adjacent North Dakota [Coal and clinker outcrop, structure contour, coal isopach, and interburden isopach maps of the Prittegurl, Pust, Elvirio, and Sears intervals], with a descriptive text, J.E. Mathews and E.M. Wilde: Montana Bureau of Mines and Geology, Geologic Map No. 50-B (map scale 1:100,000).
- Mathews, J.E., 1989d, Coal stratigraphy and correlation in the Sidney 30x60-minute quadrangle, eastern Montana and adjacent North Dakota [Paleogeographic diagrams of the Prittegurl, Pust, Elvirio, Sears, Budka, and Lane intervals], with a descriptive text, J.E. Mathews and E.M. Wilde: Montana Bureau of Mines and Geology, Geologic Map No. 50-D (map scale 1:100,000).
- May, P.R., 1954, Strippable lignite deposits, Wibaux area, Montana and North Dakota: U.S. Geological Survey, Bulletin 995-G, p. 255-292.
- Parker, F.S., 1936, The Richey-Lambert coal field, Richland and Dawson Counties, Montana: U.S. Geological Survey, Bulletin 847-C, 174 p., pl. 23-27.

- Prichard, G.E., and Landis, E.R., 1955, Geology of the northern part of the Girard coal field, Richland County, Montana: U.S. Geological Survey, Coal Investigations Map C-24, 2 sheets.
- Prichard, G.E., and Landis, E.R., 1975, Coal resources and Cenozoic geology of the Girard coal field, Richland County, Montana: U.S. Geological Survey, Bulletin 1310, 89 p.
- Spencer, J.M., 1976, Geology of the Pust lignite bed in the Burns Creek-Thirteenmile Creek Known leasing area, Dawson and Richland Counties, Montana: U.S. Geological Survey, Open-file Report 76-617.
- Spencer, M.A., 1980, Coal geology of the Girard area, Richland and Roosevelt Counties, Montana: U.S. Geological Survey, Open-file Report 80-213, 11 p., 12 pls.
- Stebinger, E., 1912, The Sidney lignite field, Dawson County, Montana: U.S. Geological Survey, Bulletin 471-D, p. 102-136.
- U.S. Geological Survey, 1976, Preliminary report of coals drillhole data and chemical analyses of coal beds in Campbell and Sheridan Counties, Wyoming; Custer, Prairie, and Garfield Counties, Montana; and Mercer County, North Dakota: U.S. Geological Survey, Open-file Report 76-319, 352 p.
- U.S. Geological Survey, 1977, Preliminary report of 1976 drilling of coals in Campbell and Sheridan Counties, Wyoming; and Big Horn, Dawson, McCone, Richland, Roosevelt, Rosebud, Sheridan, and Wibaux Counties, Montana: U.S. Geological Survey, Open-file Report 77-283, 403 p.
- U.S. Geological Survey, 1980, Coal drilling during 1978 in Big Horn, Daniels, Dawson, Musselshell, Richland, Roosevelt, Rosebud, and Valley Counties, Montana: U.S. Geological Survey, Open-file Report 80-267, 259? p.
- U.S. Geological Survey, 1981, Coal drilling during 1979 in Williams County, North Dakota, and in Beaverhead, Big Horn, Dawson, Fallon, Garfield, McCone, Musselshell, Powder River, Prairie, Roosevelt, Rosebud, and Wibaux Counties, Montana: U.S. Geological Survey, Open-file Report 81-314 , 613 p.
- U.S. Geological Survey, 1982, Coal drilling during 1980 in Big Horn, Dawson, McCone, Powder River, Prairie, Richland, Rosebud, and Treasure Counties, Montana: U.S. Geological Survey, Open-file Report 82-026 , 256? p.
- Weed, W.H., 1896, The Fort Union Formation: American Geologist, v. 18, p. 201-211.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1 Program/Project Identification No. DE-FC21-86MC10837	2 Program/Project Title Coal Science (3.5)	3 Reporting Period 4-1-92 through 8-30-92
4 Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5 Program/Project Start Date 4-1-88
		6 Completion Date 8-30-92

7 FY 91/92	8 Months or Quarters Quarters	1991 JUL AUG SEP OCT NOV DEC	1992 JAN FEB MAR APR MAY JUN																																																																																																																	
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11. Major Milestone Status	Units Planned	
	Units Complete	
A. Data Base Design	P	
	C	
	P	
	C	
B. Data Base Augmentation	P	
	C	
	P	
	C	
C. Geochemical Data Base Study	P	
	C	
	P	
	C	
D. Data Presentation	P	
	C	
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E. Annual Report	P	
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12. Remarks

Due to the EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 9 have been included.

13. Signature of Recipient and Date

[Signature] 7/23/92

14. Signature of DOE Reviewing Representative and Date

¹ Task A has been revised and performance has been extended onto FY'93.
² Task performance has been extended onto FY'93 due to the revision of Task A.

4.0 COMBUSTION RESEARCH

4.1 Atmospheric Fluidized Bed Combustion

ATMOSPHERIC FLUIDIZED-BED COMBUSTION

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

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ATMOSPHERIC FLUIDIZED-BED COMBUSTION

1.0 BACKGROUND

The main driving forces behind the use of fluidized-bed combustion have primarily been environmental concerns, fuel flexibility, and compatibility with low-cost fuels. Both bubbling and circulating designs have been developed for operation at atmospheric pressure, and many industrial-scale units of both types are currently in operation. A limited number of larger utility boilers have recently been commissioned. In addition, pressurized fluidized-bed combustion (PFBC) is making its entrance on the utility scale with the PFBC which recently began operation at the Tidd Station.

Even though fluidized-bed combustion (FBC) technologies are being commercialized, a number of areas require further research. An integrated approach should be taken toward FBC research interrelating those problems generic to bubbling, circulating, and pressurized fluidized-bed combustion systems. The program should also be designed to address specific problems related to each of these areas. Major issues facing fluidized-bed combustion are listed below:

- Methods are needed to minimize corrosion and erosion of in-bed and convective pass tubes, refractory and support surfaces, and expander turbines. Work should focus on the following:
 - Understanding mechanisms
 - ▶ Mineralogical properties of the bed and coal
 - ▶ Fluid mechanics of the bed
 - ▶ Corrosion versus erosion mechanisms
 - ▶ Stress forces on tubes
 - Assessing acceptable wastages
 - Identifying cost-effective methods of combating tube wastage
 - Developing systematic test devices
- Retrofit applications should be addressed for all types of FBCs. According to information from the American Boiler Manufacturing Association (ABMA), approximately 200 existing units are candidates for retrofit technologies. The FBC retrofits at NSP's Black Dog station, MDU's Heskett station, and Colorado Ute's Nucla station have demonstrated the feasibility of such applications.
- Fuel flexibility and characterization issues should be addressed to help users understand the constraints of fuel switching, the design considerations, and, most importantly, the economics involved in having fuel flexibility for the FBC.
- Agglomeration/sintering of bed materials and deposition on tubes, support surfaces, and refractory have been identified as problems by both manufacturers and users of FBC technology. Problem cases have been documented for both bubbling and circulating beds using a variety of fuels, including coal. The Energy and Environmental Research Center (EERC) has extensive experience in this area to help understand and solve this operational problem.

- Scaleup effects need to be addressed so that vendors and users can take pilot-scale data and be assured that the large-scale system will perform as anticipated. This database has been growing rapidly with all of the new units starting operation; however, much information is still required.
- Advanced systems should be designed to resolve problems and improve overall FBC performance. These systems should:
 - Increase the volumetric heat release rate.
 - Improve overall boiler efficiency.
 - Simplify fuel feed and ash removal systems.
 - Decrease capital and operating costs.
 - Improve turndown.
 - Decrease the size of units to enable modular construction.
- Several problems related to emissions from FBC systems need to be addressed:
 - Better sorbent utilization would improve the economics of FBC.
 - NO_x control is currently not a major problem, but could become more difficult with bubbling beds if standards become more stringent.
 - Information indicates that particulate-control problems may exist for certain types of ash. These ashes should be identified, and the use of specific equipment, conditioning, or other methods should be applied to resolve the problems.
 - Hot-gas cleanup is required for PFBC to meet turbine specifications in addition to New Source Performance Standards (NSPS).

These problems and concerns could limit FBC from reaching its full potential. Special efforts should be made to perform the necessary research to help FBC evolve into a mature technology that meets the technical, economic, and environmental needs of the future.

2.0 GOALS AND OBJECTIVES

A number of major issues have been identified that warrant further research. There are several issues in atmospheric bubbling FBC that the EERC has the capability to investigate; some of these issues are proposed in this work plan. Other FBC research should be funded, at least partially, by the industrial sector, either through the Electric Power Research Institute (EPRI) or private companies. Efforts should continue to transfer the expertise gained under previous Cooperative Agreements to the private sector.

The overall goal of the low-rank coal (LRC) FBC program at the EERC is to develop a technology database so that industry can introduce economically and environmentally acceptable coal technology options to the marketplace. Research will address those areas where data gaps exist in fuel flexibility and performance, potential operating problems, environmental compliance, advanced concepts, and system simplification.

2.1 Three-Year Objectives (7/89 - 6/92)

The EERC has developed an extensive database on the corrosion and erosion of boiler tubes, agglomeration and sintering of bed material, fuels and sorbent characterization, and particulate emissions through testing funded under the Cooperative Agreement. To successfully transfer this information to the private sector, the EERC will continue to publish results from this work at conferences and in refereed journals. The existing database will be supplemented by low-level experimentation, paper studies, economic evaluations, and surveys of operating plants and other researchers' data where needed to fill gaps.

Pilot-scale work has been performed evaluating the corrosion and erosion of boiler tube surfaces in bubbling beds. The EERC has done extensive analysis and characterization of samples generated from this testing. Over the next three years, available samples from industrial- and utility-scale boilers will be analyzed and the results correlated to bench- and pilot-scale work as well as to each other. The EERC will also attempt to obtain funding from non-DOE sources to perform more work on large-scale systems.

Efforts in corrosion and erosion will instead be focused on circulating fluidized-bed combustion (CFBC) during this time period. A pilot-scale CFBC is being constructed as part of another project. Initial work on this unit will involve system, coal, and sorbent characterization. During the characterization testing, an assessment will be made to determine if any meaningful corrosion and/or erosion data can be obtained. If meaningful data can be generated, EERC and METC personnel will discuss the possibility of incorporating CFBC corrosion and erosion work into this program.

Work will continue on the coal pretreatment cell currently being developed at the EERC. After each phase of the project, an assessment will be made to determine if the concept is still technically and economically feasible. The end result of this effort is expected to be a design of the pretreatment cell in conjunction with a bubbling and circulating FBC and an economic evaluation of the concept. Testing will be done at the pilot scale, with no demonstration planned as part of this program.

As part of the advanced concepts task and other non-Cooperative Agreement work, the EERC will work toward simplifying the control and operation of the FBC. As part of this task, users of FBC technology will be polled to identify operational problems with fuel and sorbent feed and ash removal systems. Based on priorities identified from this poll and results of other work, the EERC will work toward the simplification of control and operation of the FBC. Specific systems will be identified in either the second- or third-year work plans.

First-generation PFBC technology has reached commercialization, as indicated by the two recent Clean Coal awards for utility-scale plants. Second-generation concepts are now being developed. The success of these concepts will depend, in part, on an understanding of the effects of fuel properties on performance. The EERC will consult with developers of second-generation technology regarding the effect of fuel properties on drying, pyrolysis, combustion, and topping cycles.

The EERC is in the process of designing and constructing a pilot-scale CFBC as a part of a multiclient-funded program. This unit will be used to investigate the impact of CFBC and coal properties on performance. The test unit will not be available to this program for at least one year. Once the CFBC is available for testing, the current status of the technology will be assessed to determine if and how the unit should be incorporated into this test program.

Atmospheric fluidized-bed combustion (AFBC) has become an acceptable option for the generation of steam and electricity. A number of units are currently on-line in both the industrial and utility sector. Great market potential exists for the use of AFBC technology in both commercial and industrial sectors; however, to increase the acceptability of this technology, low cost, reliability, and ease of operation must be inherent to the system. The purpose of this task is to simplify the control and operation of the FBC for boilers in the range of 10,000 to 200,000 lb/hr. The goal of this system simplification is to make the unit easier to operate, reduce capital and operating costs, and increase the overall reliability of the system.

2.2 Proposed Third-Year Research (7/91 - 6/92)

Specific objectives of the Fluidized-Bed Combustion Project for Year Three of this three year period are as follows.

2.2.1 Task 1. Advanced Concepts--Coal Pretreatment Cell

During the past year, modifications were made to the pilot-scale pretreatment cell to allow operation under conditions that more closely simulate a full-scale unit. Also during the last program year, testing of a lignite and bituminous coal under low-temperature conditions was performed to understand and develop data under this mode of operation. Based on this preliminary information, a patent application will be prepared. Additional testing under the full range of operating conditions (temperature, air-to-fuel ratio, feed size, and residence time) will be completed using a lignite, subbituminous, and bituminous coal. The goal of this additional testing is to complete the proof-of-concept phase of the product. At the end of this program year, the coal pretreatment cell should be developed to the point where it can be marketed to commercial interests.

2.2.2 Task 2. Effects of Ash Chemistry--Corrosion/Erosion/Deposition

Understanding the impact of ash chemistry on the operation of all types of fluid beds (bubbling, circulating, and pressurized) is critical for the success of the FBC industry. To help industry understand and cope with problems related to ash chemistry, samples of corroded/eroded boiler tubes, deposits, agglomerates, sintered bed material, and other ash-related phenomena will be collected from full-scale users. These samples will be analyzed using the advanced techniques developed at the EERC, with the results correlated back to the original bed chemistry and the operating conditions of the boiler. The bed chemistry will be a function of the coal, sorbent, and bed material used, as well as operating temperature, excess air level, and residence time.

3.0 RESULTS AND DISCUSSION--COAL PRETREATMENT CELL

3.1 Equipment Description

Figure 1 shows a schematic of the EERC pilot-scale unit used for testing during the last reporting period. In the current configuration, coal is fed via a screw feeder into the coal bed approximately 26 inches above the distributor plate. A stainless steel conic section is located within the 8-inch ID coal pretreatment cell (CPC) combustor section just above the distributor plate and has the following dimensions: 24-inch length, 4-inch inlet diameter, and 8-inch outlet diameter. A combination of nitrogen and air is used as the fluidizing medium within the CPC. The addition of nitrogen allows for close control of combustion within the bed (air-to-fuel ratio) and provides additional gas volume for control of superficial gas velocity through the bed. Flue gas would be used in place of nitrogen in a commercial unit. The fluidizing gas is passed through three electric resistance heaters arranged in series within an insulated enclosure to preheat the air/nitrogen mixture to up to 1000°F, if needed, before flowing to the CPC. The fluidized bed is used in place of nitrogen in a commercial unit. The fluidizing gas is passed through three electric resistance heaters arranged in series within an insulated enclosure to preheat the air/nitrogen mixture to up to 1000°F, if needed, before flowing to the CPC.

Treated char flows by gravity from the top of the bed into a barrel. The char outlet is located approximately 4 feet above the distributor plate which, in combination with the in-bed conic section, allows for a bed volume of 1.0 ft³. Fine coal particles, moisture, and volatile gases from the fluidized bed are carried out of the CPC and into a pulverized coal test furnace. The temperature within the test furnace is maintained at

EERC# TM08140

Figure 1. Schematic of the EERC pilot-scale coal pretreatment cell.

approximately 1600°F with natural gas as fuel to ensure combustion of the fines and volatiles from the CPC. A stainless steel knockout pot with a volume of 1.5 ft³ is attached to the base of the CPC downcomer section to collect any coal fines too large to be carried through to the test furnace.

3.2 Test Procedures

A total of five tests were performed on the pretreatment cell using Blacksville bituminous coal to investigate the potential for beneficiation of the bituminous coal by simple drying only. All tests were run on feed coal having a top size of 1.25 inches. Bed inlet temperature, bed residence time (coal feed rate), and the air-to-fuel ratio (on a molar basis) were selected as independent variables for matrix testing. The superficial gas velocity through the top of the bed was set at a level high enough to maintain proper fluidization throughout the bed and to allow for a given size fraction to be retained within the CPC bed/freeboard, or to be drained through the product char outlet port. Table 1 shows the nominal test conditions under which the pretreatment cell was operated for the Blacksville bituminous coal drying tests.

3.3 Results of Blacksville Bituminous Coal-Drying Tests

Only limited results were obtained from operation of the coal pretreatment cell on the Blacksville coal. Each test period was plagued with fluidization problems due to the swelling nature of the coal. It was not possible to maintain steady-state operation for longer than about 45 minutes at any of the planned operating conditions without some type of plug occurring somewhere in the system, usually within the bed. These plugs would force either a significant increase in superficial gas velocity to reestablish fluidization, or a complete shutdown of the system to locate and clean out the problem area. Because of the operational problems encountered as a result of plugging, very little significant data were obtained from the tests that were run, and subsequent testing of the system with the Blacksville coal was discontinued.

3.4 Coal Pretreatment Cell Testing--Devolatilization Mode

Recently, two series of tests have been completed in a "devolatilization" mode of operation, one with a Beulah, North Dakota, lignite and the

TABLE 1

Blacksville Bituminous Coal Drying Tests
Nominal Test Conditions

Test Number	Inlet Temperature (°F)	Air/Fuel Ratio	Coal Feed Rate (lb/hr)
AC1-91	750	0.143	125
AC2-91	750	0.049	160
AC3-91	750	0.049	225
AC4-91	750	0.143	125
AC5-91	100	0.143	95

other with a Montana subbituminous coal. The coal pretreatment cell was operated with these two fuels at bed temperatures sufficiently high to initiate partial combustion of the fuel in the bed and allow for self-sustained operation at elevated temperatures (greater than or equal to 800°F). The purpose of the tests under these conditions is to determine the level of devolatilization of the coal; the quantity and size distribution of the char produced; and the amount of ash reduction in the product char at various levels of operating temperature, air-to-fuel ratio, and bed residence time. An overview of the results generated to date follows.

Tables 2 and 3 are the average output data and a material balance, respectively, generated from operation of the CPC on the North Dakota lignite. Included with Table 2 is a listing of the nominal test conditions under which the unit was operated. Table 2 shows that the lignite tests were run over a temperature range of about 840°-1125°F, bed residence times of 9 minutes to 18 minutes, and air-to-fuel molar ratios between 0.10 and 0.18. Calculated superficial gas velocities for the top of the expanded bed ranged from 4.4 ft/sec to about 10 ft/sec. Table 3 shows that, over the range of conditions tested, 100% of the moisture was driven out of the product char for each test, with the exception of Run CPC-BS1-0292 (99% moisture removal). The removal of volatile matter ranged from about 34% up to about 60%.

The ratio of the amount of char produced to the amount of coal fed ranged from 12% to about 40%, and there appears to be a relationship between temperature and char production, as shown in Figure 2. Char production data from three tests were plotted as a function of superficial gas velocity, and are shown in Figure 3. Operating temperature, air-to-fuel ratio, and bed residence time for each of the three tests were all similar at about 900°F, 0.10, and 11 minutes, respectively. Figure 3 suggests that, with all other conditions held constant, char production increases with increasing gas velocities. Figure 4 illustrates the relationship between the evolution of volatile matter and operating temperature. As expected, volatile matter evolution increased with increasing temperature. Figure 5 is a plot of particle-size distributions from Run CPC-BS1-0992 of various solids sampled associated with the pretreatment cell. The figure shows that the pretreatment cell is an effective solids classifier, and the size distributions of the product char and the collected fines (designated as drip leg fines) fall within rather narrow ranges.

A set of tests similar to those described above was also performed on a Montana subbituminous coal from the Colstrip Mine. The feed coal was screened prior to testing to remove the fine fraction less than 1/4 inch. The feed coal was screened to simulate more closely the size of material on which the pretreatment cell was originally designed to operate. The original design concept was to use a minimally prepared coal feedstock, possibly run-of-mine coal crushed once, and let the physical and chemical processes within the pretreatment cell reduce the average particle size and act as a classifier. The size of the product char would then be determined by specific operating conditions, such as gas velocities, temperature, residence time, and/or air-to-fuel ratio.

Tables 4 and 5 are similar to Tables 2 and 3 and show the average output data (operating conditions) and a material balance, respectively, for the Montana subbituminous coal testing. The nominal operating conditions under which the tests were performed are also listed on Table 4. As with the North

TABLE 2

North Dakota Lignite Average Output Data

Run No.	0292	0392			0492	0592		0692		0892		0992	1092
Test No.	N/A ^a	1	2	3	N/A	1	2	1	2	1	2	N/A	N/A
Average Feed Rate	117.1	121.3	121.3	121.3	182.8	199.1	199.1	233.0	233.0	173.5	173.5	168.9	181.2
TOB ^b Avg. Temp. (°F)	1075	1122	984	849	1105	840	947	990	1108	978	932	955	986
TOB Flow (acfm)	182.8	156.9	151.1	133.7	168.4	166.2	196.4	179.8	203.1	147.2	91.8	209.5	145.7
TOB SGV (ft/sec)	8.70	7.47	7.20	6.37	8.02	7.91	9.35	8.56	9.67	7.01	4.37	9.98	6.94
Fuel Input (mol/hr)	6.0	6.3	6.3	6.3	9.4	10.3	10.3	12.0	12.0	9.0	9.0	8.7	9.4
Air Input (mol/hr)	1.05	0.94	1.00	0.97	1.17	0.99	1.05	1.55	1.47	1.29	0.95	1.54	1.19
A/F Ratio (mol/mol)	0.174	0.150	0.160	0.155	0.124	0.097	0.102	0.129	0.122	0.144	0.106	0.177	0.128
O ₂ Input (%)	11.4	12.1	12.3	12.1	13.9	10.0	9.7	16.0	14.5	16.2	18.4	13.4	15.2
Avg Residence Time ^c (min)	17.93	17.31	17.31	17.31	11.49	10.55	10.55	9.01	9.01	12.10	12.10	12.43	11.59

Run No.	Test No.	Comments
CPC-BS1-0292	N/A	Test #2 scrapped due to bad odors from AFU (improper operation)
CPC-BS1-0392	1	Preheat at 300°F only.
	2	
	3	Preheat turned back up to 800°F.
CPC-BS1-0492	N/A	Preheat at 300°F only.
CPC-BS1-0592	1	Preheat at 800°F.
	2	Preheat at 300°F.
CPC-BS1-0692	1	Preheat at 300°F only.
	2	Preheat at 300°F only.
CPC-BS1-0792	N/A	Drying tests for Kerr-McGee Proposal (with M. Musich).
CPC-BS1-0892	1	Preheat at 300°F only. Adjusted ρ_s ^d from 750 to 1200 kg/m ³ .
	2	Preheat at 300°F only.
CPC-BS1-0992	N/A	Repeat BS1-0592, Test 2 with new ρ_s .
CPC-BS1-1092	N/A	Repeat BS1-0892, Test 1 with new ρ_s and. product drain extension

Nominal Conditions

Run No.	0292	0392			0492	0592		0692		0892		0992	1092
Test No.	N/A ^a	1	2	3	N/A	1	2	1	2	1	2	N/A	N/A
Bed Residence Time (min)	16.8	16.8	16.8	16.8	11.2	11.2	11.2	8.4	8.4	11.2	11.2	11.2	11.2
Feed Rate (lb/hr)	125	125	125	125	187.5	187.5	187.5	250	250	187.5	187.5	187.5	187.5
TOB Avg. Temp. (°F)	1100	1100	950	800	1100	800	950	950	1100	950	950	950	950
Product Size (in)	1/2	3/8	3/8	3/8	1/2	1/2	1/2	1/2	1/2	1/4	1/8	1/2	1/4

^a N/A - Not applicable.^b TOB - Top of bed.^c Assuming an average bulk density of 35 lb/ft³ for material within the bed and a nominal bed volume of 1.0 ft³.^d ρ_s - nominal particle density.

TABLE 3

North Dakota Lignite Material Balance

Run No.:	0292	0392			0492	0592		0692		0892		0992	1092
Test No.:	N/A	1	2	3	N/A	1	2*	1	2	1	2	N/A	N/A
Run Duration, min	84.0	197.8	197.8	197.8	59.8	135.0	135.0	140.1	140.1	125.2	125.2	89.5	61.6
Test Duration, min	60.0	60.0	60.0	60.0	56.0	71.8	60.0	69.6	60.0	60.4	50.0	84.7	56.9
Coal Fed per Run, lb	164.0	400	400	400	182	448	448	544	544	362	362	252	186
Average Feed Rate, lb/hr	117.1	121.3	121.3	121.3	182.8	199.1	199.1	233.0	233.0	173.5	173.5	168.9	181.2
Product Char Collected, lb	14	30	34	45	51.5	89.8	95	85.5	47	38	43	51	47
Drip Leg Fines Collected, lb	25	23	18	14.5	20.5	22.5	19.7	46.5	43.0	35.5	17	77	23
Product Moisture Content, %	0.2	0	0	0	0	0	0	0	0	0	0	0	0
Product Volatile Content, %	20.95	19.24	22.16	27.64	18.70	28.80	23.98	23.00	17.57	22.84	25.47	23.18	24.55
Avg. Moisture Loss, lb	22.3	23.4	23.4	23.4	32.8	45.9	38.3	52.0	44.9	33.6	27.8	45.9	33.1
Avg. Volatile Matter Loss, lb	26.6	29.7	26.1	19.5	42.6	35.5	39.2	55.9	60.9	36.4	26.4	48.9	32.9
Avg. Moisture Loss, %	98.96	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Avg. Volatile Matter Loss, %	52.05	55.96	49.28	36.74	57.20	34.08	45.11	47.36	59.78	47.72	41.70	46.94	43.81
Total Accountable, lb	88.0	106.0	101.5	102.3	147.5	193.7	192.3	239.9	195.7	143.6	114.2	222.8	136.0
Closure, %	75.1	87.4	83.6	84.3	86.4	81.3	96.6	88.8	84.0	82.2	78.9	93.5	79.1
Uncollected Fines (calc.), lb	29.2	15.3	19.9	19.0	23.1	44.7	6.8	30.3	37.3	31.2	30.4	15.6	35.9
Total Fines, lb	54.2	38.3	37.9	33.5	43.6	67.2	26.5	76.8	80.3	66.7	47.4	92.6	58.9
Product Char d_{50} , micron	5025	4989	4888	6632	4759	4653	5279	4208	4601	4945	4761	4987	4187
Product Char d_{90} , micron	1949	2107	2040	2457	1919	1777	2090	1690	1913	2136	1881	1962	1662
Product Char d_{10} , micron	788	790	784	744	806	751	859	776	841	978	640	894	801
Bed Material @ EOR, lb	10	N/A	N/A	8.5	9	N/A	16.5	N/A	?	N/A	?	?	?
Char/Feed Ratio, %	12.0	24.7	28.0	37.1	30.2	37.7	47.7	31.6	20.2	21.7	29.7	21.4	27.4
Drip Leg Fines/Feed Ratio, %	21.3	19.0	14.8	12.0	12.0	9.4	9.9	17.2	18.5	20.3	11.8	32.3	13.4
Uncoll. Fines/Feed Ratio, %	24.9	12.6	16.4	15.7	13.6	18.7	3.4	11.2	16.0	17.8	21.1	6.5	20.9
Total Fines/Feed Ratio, %	76.0	96.7	97.0	106.6	80.9	71.8	96.2	64.5	56.2	68.8	84.3	60.6	73.4

* The "Product Char Collected" value for Run BS1-0592, Test 2 is a best-guess estimate.

Figure 2. The ratio of char to coal feed as a function of operating temperature for the North Dakota lignite devolatilization testing.

Figure 3. The ratio of char produced to coal fed as a function of superficial gas velocity for the North Dakota lignite devolatilization testing.

Figure 4. Volatile matter evolution as a function of operating temperature for the North Dakota lignite devolatilization testing.

Figure 5. Particle-size distributions for various solid samples taken during North Dakota lignite Test CPC-BS1-0992.

Dakota lignite tests, the Montana subbituminous coal was tested at temperatures ranging from about 850° to 1075°F. Three additional simple drying tests were run at the conclusion of the devolatilization tests to determine the level of beneficiation possible with this type of coal at relatively low temperatures. The operating temperatures for these tests ranged from about 250° to 520°F.

Bed residence times and air-to-fuel ratios similar to those used for the lignite testing were employed for the subbituminous coal tests and ranged from 8 minutes to 19 minutes and between 0.10 and 0.20, respectively. Calculated superficial gas velocities for the top of the expanded bed were generally higher for the subbituminous coal tests because of the larger feed-coal size and ranged from 6.9 ft/sec to about 11.4 ft/sec. Table 5 shows that, over the range of conditions tested, 100% of the moisture was driven out of the product char for each test, with the exception of the simple drying tests, i.e., those tests under the run number designation CPC-MT1-1492 (89% to 98% moisture removal). The removal of volatile matter ranged from less than 1% to about 14% for the drying tests, and from 40% up to about 57% for devolatilization testing. The ratio of the amount of char produced to the amount of coal fed ranged between 21% and about 40% for the devolatilization mode of testing, and 33% to 52% during the drying tests.

A more complete analysis of the data is currently underway, and a comprehensive final report covering the results of the pretreatment cell testing is in preparation.

TABLE 4

Montana Subbituminous Coal^a Average Output Data

Time-Weighted Averages										
Run No.	Test No.	Average Feed Rate (lb/hr)	TOB ^b Avg. Temp. (°F)	TOB Flow (acfm)	TOB SGV (ft/sec)	Fuel Input (mol/hr)	Air Input (mol/hr)	A/F Ratio (mol/mol)	Oxygen Input (%)	Avg. ^c Residence Time (min)
CPC-MT1-1192	1	204.6	935	195.48	9.31	12.0	1.55	0.129	14.2	10.26
	2	204.6	947	157.40	7.50	12.0	1.20	0.100	13.8	10.26
CPC-MT1-1292	1	180.8	968	238.70	11.37	10.6	1.74	0.164	13.3	11.62
	2	180.8	856	175.50	8.36	10.6	1.08	0.102	10.4	11.62
CPC-MT1-1392	1	211.5	1076	212.66	10.13	12.4	1.54	0.124	14.3	9.93
	2	111.1	972	207.82	9.90	6.5	1.23	0.189	10.8	18.90
	3	111.1	911	215.75	10.27	6.5	1.30	0.199	10.6	18.90
CPC-MT1-1492	1	130.1	518	160.63	7.65	7.6	1.25	0.163	9.9	16.14
	2	130.1	299	145.11	6.91	7.6	1.03	0.135	6.9	16.14
	3	254.7	254	157.49	7.50	14.9	2.11	0.141	12.3	8.24

NOMINAL CONDITIONS:

Run No.	Test No.	Residence Time (min)	Feed Rate (lb/hr)	TOB Avg. Temp. (°F)	Product Size (in)	Comments
CPC-MT1-1192	1	11.20	187.5	950	3/8	Preheaters on.
	2	11.20	187.5	950	1/4	Preheat at 300°F only.
CPC-MT1-1292	1	11.20	187.5	950	1/2	Fluidization problems.
	2	11.20	187.5	800	1/4	Lost fluidization @ bottom of bed.
CPC-MT1-1392	1	11.20	187.5	1100	3/8	
	2	16.80	125	950	3/8	Preheat at 300°F only.
	3	16.80	125	950	3/8	Preheaters up to 800°F.
CPC-MT1-1492	1	16.80	125	N/A	3/8	Relatively low-temperature drying test.
	2	16.80	125	N/A	3/8	Repeat of MT1-1492 Test 1 with lower bed temperatures.
	3	8.40	250	N/A	3/8	Drying test at higher feed rate.

^a All feed coal was sized to +1/4" prior to testing.^b TOB - Top of bed.^c Assuming an average bulk density of 35 lb/ft³ for material within the bed and a nominal bed volume of 1.0 ft³.

TABLE 5

Montana Subbituminous Coal Material Balance

Run No.:	MT1-1192	MT1-1192	MT1-1292	MT1-1292	MT1-1392	MT1-1392	MT1-1392	MT1-1492	MT1-1492	MT1-1492
Test No.:	1	2	1	2	1	2	3	1	2	3
Run Duration, min	143.7	143.7	179.9	179.9	73.2	143.7	143.7	105.2	105.2	38.2
Test Duration, min	61.7	64.8	63.6	70.7	70.0	63.3	72.2	69.2	36.0	38.2
Coal Fed per Run, lb	490	490	542	542	258	266	266	228	228	162
Avg. Feed Rate, lb/hr	204.6	204.6	180.8	180.8	211.5	111.1	111.1	130.1	130.1	254.7
Product Char Collected, lb	62	75	51	72	52.5	25	54	71	26	84
Drip Leg Fines Collected, lb	48	20.5	51.5	13.5	39	22	24.0	5.1	3.5	15.0
Product Moisture Content, %	0	0	0.	0	0	0	0	0.5	1.7	2.7
Prod. Volatile Content, mf, %	23.31	22.11	24.48	18.69	21.47	26.13	21.68	37.25	42.83	41.00
Avg. Moisture Loss, lb	52.5	55.2	47.8	53.1	61.6	29.2	33.3	36.7	18.1	36.0
Avg. Volatile Matter Loss, lb	42.0	46.8	36.0	52.3	53.8	20.1	28.8	9.0	0.3	3.7
Avg. Moisture Loss, %	100.00	100.00	100.00	100.00	100.00	100.00	100.00	98.00	93.19	89.18
Avg. Volatile Matter Loss, %	46.12	48.89	43.41	56.80	50.37	39.60	49.88	13.89	0.99	5.22
Total Accountable, lb	204.4	197.4	186.2	190.9	206.8	96.3	140.2	121.8	48.0	138.7
Total Accountable w/ Bed Mat'l, lb					219.8			142.8	74.5	164.7
Closure, %	97.2	89.3	97.3	89.7	83.8	82.2	104.9	81.2	61.5	85.6
Closure w/ Bed Material, %					89.1			95.2	95.4	101.7
Uncollected Fines (calc.), lb	5.9	23.7	5.2	22.0	39.9	20.9	-6.5	28.2	30.1	23.3
Total Fines, lb	53.9	44.2	56.7	35.5	78.9	42.9	17.5	33.3	33.6	38.3
Bed Material @ EOR, lb	N/A	28.5	N/A	20.9	13	N/A	13	21	26.5	26
Char/Feed Ratio, %	29.5	33.9	26.6	33.8	21.3	21.3	40.4	47.3	33.3	51.9
Drip Leg Fines/Feed Ratio, %	22.8	9.3	26.9	6.3	15.8	18.8	18.0	3.4	4.5	9.3
Uncoll. Fines/Feed Ratio, %	2.8	10.7	2.7	10.3	16.2	17.8	-4.9	18.8	38.5	14.4
Total Fines/Feed Ratio, %	25.6	20.0	29.6	16.7	32.0	36.6	13.1	22.2	43.0	23.6

13. Signature of Recipient and Date <i>Chris Henderson for Michael D. Young</i>	14. Signature of DOE Reviewing Representative and Date
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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Atmospheric Fluidized-Bed Combustion (4.1)		3. Reporting Period 3-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Advanced Concepts--Coal Pretreatment Cell:				
a.1	Complete test matrix on lignite coal	9-30-91	12-31-91		
a.2	Complete test matrix on subbituminous coal	12-31-91	5-30-92		
a.3	Complete test matrix on bituminous coal	3-31-92	3-31-92		
a.4	Proof-of-concept with design information for full-scale plant	6-30-92			
Task B	Effects of Ash Chemistry--Corrosion/Erosion/Deposition:				
b.1	Obtain and analyze materials	3-31-92	3-31-92		
b.2	Correlate data	6-30-92	*		
* No special analysis were requested.					

4.2 Beneficiation of Low-Rank Coals

BENEFICIATION OF LOW-RANK COALS

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

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BENEFICIATION OF LOW-RANK COALS

1.0 GOALS AND OBJECTIVES

The overall objectives of the Low-Rank Coal Beneficiation Project are to study methods to reduce the inorganic content and increase the heating value of low-rank coal (LRC) to produce high-quality dry fuels and/or coal/water fuels (CWF). The Energy and Environmental Research Center (EERC) has previously demonstrated with a 600-lb/hr continuous pilot plant that hot-water drying (HWD) of lignite or subbituminous coal can produce high-energy content, dry or slurry fuels. Integration of continuous chemical and physical cleaning processes with HWD can produce low-ash, low-moisture CWF suitable for advanced combustion systems.

Presently the LRC Beneficiation Project is continuing the development, on the bench scale, of a LRC agglomeration process which combines a chemical cleaning step with an aggregation step using coal-derived oil. Previous statistical testing has studied the effects of major variables on agglomerate qualities. The variables studied included coal particle size, acid concentration, acid mixing speed and acid contact time, and oil mixing speed and oil mixing time. The process has been proven effective with all coals tested including North Dakota and Texas lignites, and Alaska, Wyoming, and Montana subbituminous coals. A limited amount of testing had been performed on deoiling techniques to recover agglomerating oil for recycle or resale as an upgraded, light oil fraction.

The proposed third-year research efforts for oil agglomeration (Task A) as described in the Sixth Annual Program Plan were:

1. Agglomeration with Carrier Solvent - Testing will determine if LRCs can be agglomerated when the agglomerating oil is dissolved in a carrier solvent. The carrier solvent ideally would aid in dispersion of the oil on the coal and reduce the quantity of oil for agglomeration. Reducing the quantity of oil could eliminate the deoiling step. The carrier solvent would be recoverable from the wastewater and agglomerates for recycle. Carrier solvents will be tested that are compatible with both coal- and petroleum-derived oils.
2. Recycle and Makeup Requirements - Analytical techniques will be tested to determine the oil content of agglomerates and wastewater. Similarly, analytical techniques will be developed to determine the residual acid concentration in the wastewater. Wastewater will be recycled to determine if the presence of soluble cations will deleteriously affect the ash content of the acid-cleaned or agglomerated coal. The determination of oil and acid consumption will allow estimation of preliminary economics and equipment sizing for process scaleup.
3. Process Modifications for Agglomerate Formation and Dewatering - Agglomeration aids will be tested which can provide the ionic strength required for agglomeration. The agglomeration aids could eliminate or reduce acid use when inorganic reduction is not

essential but dewatering is still desired. Also, briquetting will be tested as a method of compacting the oil/coal mixture when agglomeration is not successful. A pellet or briquette could be made having the characteristics of successfully agglomerated coal.

4. Mass Agglomerate Formation and Deoiling Techniques - The batch agglomeration process will be tested on a slightly larger scale in order to minimize the agglomeration experiments required to produce material for deoiling and product stability testing. Techniques will be further investigated to determine the appropriate conditions and method for agglomerate deoiling.
5. Development of Agglomerate Stability Analysis Techniques - Analysis techniques will be tested to determine chemical and physical stability. Stability parameters of importance are crushing strength, durability, abrasion resistance, water immersion resistance, and freeze/thaw resistance. Chemical stability will address resistance to oxidation and spontaneous combustion.

Additional beneficiation techniques described in Task B include froth floatation and colloidal coal cleaning. Techniques will be tested which aid in increasing the floatability of LRCs, and the chemical solubilization of coal humates will be tested as a method of producing low inorganic-content fuels.

2.0 ACCOMPLISHMENTS

Progress was made toward addressing Tasks A.2, A.3, and A.4 and Task B.1. Analytical techniques for determining the oil content of agglomerates and process water were evaluated by agglomerating a lignite and a subbituminous coal with crude phenol/tar oil and then performing oil, moisture, and solids balances. The analytical techniques include azeotropic distillation and Soxhlet extraction for determining agglomerate moisture and oil contents, respectively, and total carbon to determine the oil content of the process water. Several improvements were made to the agglomerate oil measurement technique and the resulting balance closures indicated that the analysis methods are not grossly in error.

Additional agglomerating oils were tested, with varying degrees of success, in the EERC agglomeration process. The oils tested included a commercial cresylic acid, liquefaction-derived oils, mild gasification-derived tars, and used motor oil. The ability of the oils to agglomerate easily at low-shear mixing conditions was qualitatively correlated against the polar and oxygen contents of the oils. Preliminary results indicate that the high polar and oxygen content oils are easily agglomerated at low-shear conditions while the low polar and oxygen content oils require high-shear mixing or surfactants to promote agglomerate formation. The determination of oxygen and polar content may progress into a screening method for determining candidate LRC agglomerating oils.

Several tests indicated that the acid precleaning step may be eliminated when inorganic reduction is not necessary. Alkali and alkaline earth metal salts successfully replaced the acids during agglomeration by, hypothetically,

providing the necessary solution ionic strength. Carbonic acid also successfully promoted agglomeration at an ionic strength 10^{-3} to 10^{-4} of nitric, sulfuric, or hydrochloric acids. Persistence in testing paid off when the crude phenol/tar oil successfully agglomerated the Beulah lignite without a prior acid-cleaning step or the addition of acid or metal salt during the agglomeration step.

The EERC agglomeration process was scaled up from 50 g of coal per test to 200 g of coal per test to allow production of large quantities of agglomerates for deoiling and strength and stability tests. The process was scaled up further, resulting in the successful agglomeration of 2.5 kg of coal in a 5-gallon pail.

Agglomerate deoiling tests with a batch autoclave have resulted in inefficient oil removal and poor temperature control. Preliminary tests with a batch fluid-bed reactor have indicated that this system may be ideal for thermally deoiling agglomerates. The hydrodynamics of the fluid bed provide excellent temperature control using either an inert gas or steam as a deoiling/fluidizing medium. The fluidizing action was not severe enough to cause significant agglomerate degradation. Presently the system is limited by its small agglomerate capacity and slightly inefficient condensate-recovery system.

Additional tests conducted during the period of January through June 1992 included:

1. Removal of soluble oil from the process water by solvent extraction.
2. Removal of soluble oil from the process water by absorption on coal.
3. Durability testing of air-dried and oven-dried agglomerates.

3.0 INTRODUCTION

LRCs (lignitic, subbituminous, and brown) are characterized by a number of qualities which make them ideal for combustion and/or conversion processes. The inherent alkali content and high volatile-matter content of the LRCs make them ideally suited as a gasification feedstock. The low-sulfur content of some subbituminous coals makes them compliance coals for power generation. Additionally, most LRCs are low in ash and are inexpensively strip-mined. Even though these LRCs are plentiful in southern coast states, between the Mississippi River and the Rocky Mountains, and, most certainly, in Alaska, their marketability has been restricted by their high moisture and, consequently, low energy contents. Additionally, the fouling problems associated with the high sodium content have inhibited the use of some LRCs. Considerable effort has been put forth to develop processes which increase energy content and reduce mineral content, yet produce a competitively priced feedstock from LRCs.

Although oil agglomeration of bituminous coals has been conducted for many years, the extension of these techniques to LRCs had achieved limited success, until recently. The primary reason for the inability to agglomerate LRCs lay in the incompatibility of the agglomerating oil and the coal surface.

The low moisture and low exchangeable-ion contents plus relatively few oxygen functionalities make bituminous coals compatible with nonpolar oils. The converse is true for the LRCs in that the high moisture content, oxygen functionalities, and cations make nonpolar oils unsuitable for agglomeration. Polar, coal-derived oils, however, can be used to agglomerate LRCs, and the polar oils are aided by surface modification and high ionic-strength aqueous treatment. Surface modification consists of removing the cations which contribute to the hydrophilicity and consequent oleophobicity of the coal. The cation (ash) level of the coal can be reduced by aqueous phase ionic exchange. Simultaneously, the high ionic strength of the low-pH solution is theorized to establish a concentration gradient between the water in the coal capillaries and the bulk water of the aqueous solution. This concentration gradient allows the polar oils, which are more compatible with the oxygen functionalities, to displace the capillary water. The agglomerating oil also thinly covers the carbonaceous material on the coal surface, and, as a result of mixing, the oil-covered surfaces come into contact and aggregate together. The aggregate size can be controlled by the speed of mixing, the amount of agglomerating oil, and the agglomeration time.

The EERC has demonstrated that low-ash fuel can be produced by a combination of physical cleaning followed by chemical cleaning of fine coal. Laboratory testing has reduced LRC ash contents to less than 1 wt% using float/sink techniques followed by dilute acid leaching (1). LRCs with ash contents as low as 2 wt% have been produced on the pilot scale using dense-media separation followed by continuous acid leaching (2,3). Each method has also shown that the sodium content can be significantly reduced. These processes, however, produce a clean coal which would be restricted to utilization at a site adjacent to the preparation facility. The hazards associated with finely ground coal, such as dustiness and oxidation, would prohibit long-range transport of this form of beneficiated coal. However, the EERC has demonstrated that a process of dilute acid leaching followed by oil agglomeration accomplishes similar ash reductions and, equally important, produces a low-moisture, high heating-value LRC with the potential to be easily transported and resistant to weathering.

4.0 AGGLOMERATION DEVELOPMENT AND TESTING

4.1 Agglomeration Experimental Procedure

The EERC agglomeration procedure is divided into two steps: acid cleaning followed by oil agglomeration. The same sample cell is used throughout the process. The coal is pulverized to a top size of 30 mesh prior to agglomeration, with the agglomerates being recovered on a 30-mesh screen. All the steps in the process are carried out at room temperature and atmospheric conditions. Table 1 contains the experimental parameters needed to achieve agglomeration. The acid-cleaning (leaching) step consists of mixing a quantity of coal with a quantity of dilute acid solution, typically using 1 part coal to 2 parts of a dilute acid solution. The coal/acid solution is stirred for 1 to 30 minutes, typically less than 5 minutes, at a speed of 5500-6000 rpm in a high-shear mixer.

TABLE 1
Oil Agglomeration Experimental Parameters

Coal Particle Size	less than 30 mesh by 0
Acid Concentration	6.0, 3.0, 1.5, and 0.75 wt%
Acid-Cleaning Speed	5500 - 6000 rpm
Acid-Contact Time	1 - 30 minutes
Oil-Mixing Speed	600 - 800 rpm
Oil-Mixing Time	5 - 10 minutes

Agglomeration consists of adding a quantity of agglomerating oil, typically equivalent to the weight of the coal, to the coal/acid solution. The sample is mixed using a low-speed T-bar mixer until agglomeration occurs. Agglomeration is normally indicated by a change in solution turbidity. The raw agglomerates are recovered on the 30-mesh screen, and the coal that passes through the screen is recovered by filtration using a Buchner funnel and filter paper. The agglomerates are washed, and the samples are allowed to air-dry overnight prior to weighing and analysis. Figure 1 is a representation of the agglomeration process.

The raw coal moisture and solids contents are determined according to ASTM D3173. The agglomerating oil moisture content is determined by Karl-Fischer analysis and ash content is determined by proximate analysis according to ASTM D3174. The agglomerating oil carbon content is determined from ultimate analysis by ASTM D3176. The process water is analyzed by Standard Method No. 505A to determine total carbon content, in mg/L (4). The total soluble oil content in the process water is calculated as follows:

$$\text{Total Soluble Oil Content (mg/L)} = \frac{\text{Process Water Total Carbon Content (mg/L)}}{\text{Oil Carbon Content (wt\%)} \times 100}$$

The composition (i.e. wt% carbon) of the soluble oil is assumed to be equivalent to that of the agglomerating oil composition.

The moisture contents of raw, air-dried, or oven-dried agglomerates are determined by azeotropic distillation with xylene, and oil contents are determined by Soxhlet extraction with methylene chloride (5). The tailings are analyzed using the agglomerate analysis techniques if sufficient quantities are produced.

Oil, water, and solids balances are calculated using the weights and compositions of the raw agglomerates and raw tailings. The raw agglomerate moisture is always directly determined by azeotropic distillation. However, the oil content of the raw agglomerates is either directly determined by Soxhlet extraction or calculated from analysis of the air- or oven-dried agglomerates. Consequently, four separate methods can be used to determine the raw agglomerate oil content. Method 1 determines the raw agglomerate oil

Figure 1. Schematic diagram of the EERC oil agglomeration process.

content directly by Soxhlet extraction. Method 2 calculates the raw agglomerate oil content based on the air-dried agglomerate moisture and oil contents. Method 3 calculates the raw agglomerate oil content based on the oven-dried agglomerate moisture and oil contents. Method 4 calculates the raw agglomerate oil content based on the air- and oven-dried agglomerate moisture and oil contents. The analysis sequence for determining the moisture and oil contents of the raw agglomerates is illustrated in Appendix A.

The oils tested in the agglomeration process are each analyzed to determine oxygen and polar oil content. The oxygen and polar contents are correlated with the effectiveness of the oil to promote agglomeration.

The agglomerating oil oxygen content is determined by difference from ultimate analysis by ASTM D3176. The polar oil content is determined by open column chromatography using silica gel (-28 x +200-mesh) activated by oven-drying at 250°C for 2 hours. The linear and small aliphatics are eluted from the oil sample using pentane; isooctane was used to elute branched and large aliphatics; methylene chloride was used to elute aromatics; methanol was used to elute the polars. The extracting solvents are evaporated to recover the oil fractions. The total mass of recovered oil is determined for each test to assess the efficiency of extraction and to calculate a mass balance closure.

4.2 Results and Discussion

4.2.1 Agglomeration Process Scale-up

The amount of coal that can be agglomerated using the EERC oil agglomeration process was increased from 50 to 200 g per test. This was done

in order to produce enough agglomerates to satisfy requirements for analytical testing techniques such as oil content measurements, stability testing, and deoiling for oil recovery. The major changes that were necessary in order to accomplish scale-up were increases in vessel size and tip-to-tip width of the T-bar mixer. A total of 14 tests were conducted using crude phenol/tar oil agglomerant and 200 g of coal. The first two tests, using 200 mL of oil, failed to form agglomerates, presumably because of an excess of agglomerant. Successful agglomeration was achieved after reducing the agglomerant quantity from 200 mL to 180 or 190 mL. Additional operational changes were made to reduce the amount of tailings (-30-mesh agglomerates). Mixing speed (shaft rpm) reduction was sufficient to allow the small agglomerates to grow larger than 30 mesh. At comparable shaft speeds the larger T-bar mixer had a higher tangential tip speed that was presumed to inhibit agglomerate growth. Consequently, the tailings produced from 180 mL of oil and 200 g of coal were proportional to using 50 g of coal and 50 mL of oil.

Following the success of this scale-up, two agglomeration tests were performed in which the coal was agglomerated in a 20-liter pail. A T-bar mixer was fabricated using the same tip-to-tip ratio as that employed in the 200-gram mixer. The first test was performed using approximately 2700 g of coal and crude phenol/tar oil and 5400 g of 0.63 M nitric acid solution. A 1/4-horsepower mixer was mounted on a special pail lid to drive the T-bar mixer. The test produced about 450 g of +30-mesh, air-dried agglomerates; however, a vast majority of the coal was an oily mass. Upon termination of the experiment, it was observed that a large quantity of coal was on the bottom of the pail, presumably a consequence of the T-bar mixer not extending far enough into the pail to allow thorough mixing. It was also concluded that the tip speed was slightly high; therefore, the oil and coal contact was too fast to promote agglomeration. Another experiment was attempted following the modifications to the mixer. This experiment used approximately 1500 g of coal and crude phenol/tar oil and 3000 g of 0.63 M nitric acid solution. A smaller quantity was used because the bucket was too full with the earlier experiment. The shaft speed was reduced from the previous experiment. This test very successfully produced approximately 2000 g of agglomerates. A small quantity of agglomerates were lost during washing on a 30-mesh screen. To perform more agglomeration testing in the 20-liter pail, it will be necessary to utilize much more efficient methods to recover the agglomerates because a considerable amount of water was necessary to wash the fines from the agglomerates.

4.2.2 Testing of Additional Agglomerating Oils

Several additional coal- and petroleum-derived oils were tested as agglomerants in the EERC oil agglomeration process. These oils included commercially produced cresylic acid No. 83 black (CA83BL), generically known as alkylated phenols, from the Merichem Company of Houston, Texas; two liquefaction-derived oils from run #263J at Wilsonville, Alabama; two mild gasification-derived tars from the EERC mild gasification project; and used 10W-40 crankcase oil.

4.2.2.1 Cresylic Acid

Successful agglomeration using cresylic acid was only possible after the oil content was reduced from 50 mL (standard with crude phenol/tar oil) to as low as 30 mL per 50 g of coal. At oil volumes above 30 to 35 mL, an oily mass

or clumped agglomerates were formed. However, to achieve agglomeration at these lower agglomerant volumes, low-shear mixing had to be increased from the traditional 2 to 5 minutes to as long as 7 to 15 minutes. Successful agglomeration also occurred when the majority of CA83BL was added during high-shear mixing. This resulted in almost immediate agglomerate formation, and slight agglomerate growth was achieved with low-shear mixing and slight oil addition. The high-shear mixing resulted in almost no tailings production although the +30-mesh agglomerates were smaller than typically formed agglomerates. Agglomerates produced from this oil had physical characteristics similar to the agglomerates produced using crude phenol/tar oil.

4.2.2.2 Liquefaction Oils

The liquefaction oils numbered V161 and V178 were produced at the liquefaction plant by distilling the "raw liquefaction product." Both oils are classified as light oils or naphthas by Wilsonville. The V161 is 45.9 wt% of the product, a light fraction with over 97 wt% boiling under 550°F. The V178 is 54.1 wt% of the product, a heavier fraction with over 85 wt% boiling in the range of 550°F to +850°F.

Five agglomeration tests were conducted with V161, with four tests being considered successful. The single failure was based on the traditional agglomeration methods employed when using crude phenol/tar oil. This oil could agglomerate the coal at volumes as low as 30 mL when a surfactant such as Triton X-100 (2 g/50 g coal) or crude phenol (10 g/50 g coal) was used. Also, a single test produced the results that, during high-shear mixing, the oil requirements could be reduced.

The agglomeration tests performed with V178 oil used a surfactant to help promote agglomeration. The surfactant was chosen based on the results with the V161 oil. One test used 2 g Triton X-100 to 50 g coal, and the other used 5 g crude phenol to 50 g coal. The volume of V178 oil ranged from 25 to 30 mL with no tailings production during either test. The agglomerates produced from these two oils appeared to be very brittle after air-drying, compared to the crude phenol/tar oil agglomerates.

4.2.2.3 Mild Gasification Tar

Two mild gasification tars were used for agglomeration testing. The first tar tested was from the knockout pots, and the other one was from the back cyclone of the mild gasification unit. The knockout pot tar appeared to contain a considerable amount of very fine coal that was probably blown over during the fluidization process. Neither of the tars mixed well with water or flow at room temperature so they were thinned in a variety of solvents. The best solvent for thinning the knockout pot tar was butanol; for the back cyclone tar, it was pentane. A 60:40 wt% knockout pot tar/butanol mixture did not form agglomerates using normal low-shear mixing methods. Similarly, an 83:17 wt% back cyclone tar/pentane mixture did not form agglomerates under typical agglomerating conditions. However, after mixing the tar/pentane mixture under high-shear conditions, agglomerates were formed using 36 g of the mixture per 50 g coal. The sample was placed under the low-shear mixer to

promote agglomerate growth. These agglomerates were extremely small compared to the normal agglomerates, probably due to the high-shear mixing that was employed.

4.2.2.4 Used Crankcase Oil

Using normal agglomerating conditions with a sample of 10W-40 used crankcase oil was unsuccessful at producing agglomerates. However, high-shear mixing of this sample caused a distinct phase separation. Phase separation is an indication that the coal is preferentially wetted by oil and no longer dispersed in the water phase. Since there is no oil dispersed in the water phase, oil recovery could be easy if agglomeration were performed with crankcase oil.

The high-shear mixing results presented above were employed using incremental addition of oil until phase separation was observed. Following the phase separation, the oil/water/coal was mixed with the low-shear mixer until agglomeration was complete. The test was repeated by adding the oil in a single dose during high-shear mixing. Once again agglomeration was successful with only 13 mL of oil required to agglomerate 50 g of coal. This compares with approximately 45 to 50 mL of crude phenol/tar oil to agglomerate 50 g of Beulah lignite.

4.2.3 Ionic Strength Modification Testing

It was hypothesized that other sources of ionic strength may be just as effective as dissociating acids, i.e., nitric acid. Investigations were done to verify this by using potassium nitrate, calcium acetate, and carbonic acid as sources of ionic strength.

A 1 M solution of potassium nitrate was used for a source of ionic strength in the agglomeration process. The initial solution was made by mixing potassium hydroxide with nitric acid. The solution pH was adjusted to 4.0, much higher than normally achieved during agglomeration. Agglomeration was performed using the normal agglomerating conditions. The experiment was successful with only slight bridging of agglomerates. Several more experiments were performed using another solution of potassium nitrate that was made using potassium nitrate crystals. The pH of this 1 M solution was 6.7. Agglomeration was very successful with this solution using 45 mL of oil. The success of potassium nitrate led to the use of calcium acetate as an ionic solution. This test was also successful with the conditions employed using potassium nitrate in the agglomeration process.

Carbonic acid was used as a source of ionic strength because of the low cost of producing it compared to nitric acid. The carbonic acid source for this testing was carbonated sparkling water. Normally the carbonic acid could be produced by bubbling carbon dioxide in water. The original pH of the sparkling water was 4.6, and it increased to 5.9 after acid cleaning. Agglomeration was carried out in the normal manner with very few fines produced. This test shows that inexpensively produced carbonic acid could be used for agglomeration when little, if any, inorganic reduction is required.

4.2.4 Agglomeration Without Coal-Surface Modification

Several tests were performed without acid cleaning or surface modification of the coal. These tests were done using crude phenol/tar oil as the agglomerant. The first test performed with Beulah lignite was done using incremental oil addition until agglomeration was observed. This test required a quantity of 40 mL oil for agglomeration to occur. The agglomerates produced were very tiny. This successful test led to another test where the oil was added all at once in the normal manner. Agglomeration was very successful with very little fines production. Oil agglomeration conditions were optimized because testing was performed using 30-50 mL oil. At 30 mL, small agglomerates were formed, but they were much smaller than the required 30-mesh size. For 50 mL, the agglomerates formed were oil-bound and clumped together. Duplicate analysis using 40 mL oil produced the same results as the successful initial testing.

4.2.5 Characterization of Agglomerating Oils

The ultimate analysis results of the agglomerating oils are presented in Table 2, and the aliphatic, aromatic, and polar contents are presented in Table 3. The agglomerating oils tended to increase in oxygen content as the polar content increased, although the oil with the highest oxygen content did not have the highest polar content. Similarly, the oil with the lowest oxygen content did not have the lowest polar content. Preliminary review of the analyses suggests that there may be a correlation between the composition of the oil and its ability to promote agglomeration. The oils with the highest oxygen and polar contents tended to be the most suitable for agglomeration at low-shear conditions. Conversely, the oils with lower oxygen and polar contents required high-shear mixing or the addition of surfactants to promote agglomeration.

The preliminary results of oxygen- and polar-content analyses suggest these techniques can be used for screening candidate oils for LRC agglomeration. However, because of the length of time required to generate these analyses, the applicability of an oil for agglomeration may be more quickly determined by performing agglomeration experiments. Consequently, determination of oxygen and polar contents may be used to substantiate why a particular oil did not work at low-shear conditions, but instead required high-shear mixing or surfactants.

4.2.6 Moisture, Oil, and Solids Balances

Three agglomeration balance tests were performed, two with Beulah lignite and one with Spring Creek subbituminous coal. The balance tests were similar to the one discussed in the July-December 1991 semiannual when m-cresol was used as the agglomerating oil (6). The balances differed primarily in the calculation method for the raw agglomerate oil content.

The agglomerating oil used in each test was a 94/6 vol% blend of coal-derived crude phenol and tar oil, each obtained from the Dakota Gasification Company, Beulah, North Dakota. The analyses of the two coals are presented in Table 4.

TABLE 2

Ultimate Analysis Results for Agglomerating Oils, wt%

	Phenol/ Tar Oil	Cresylic Acid	Mild Gas Tar	Used Motor Oil	V-161	V-178	V-1074	ROSE Resid
As-Determined Moisture	5.39	0.17	21.82	0.18	0.50	0.08	1.38	0.15
Moisture-Free Carbon	77.02	79.18	88.25	84.31	84.43	87.64	89.93	89.95
Hydrogen	6.91	8.67	8.71	12.95	12.00	10.17	9.14	7.24
Nitrogen	1.04	0.16		0.46	0.49	0.89	0.83	1.13
Sulfur	0.03	0.00	0.17	0.60	0.00	0.00	0.00	0.00
Oxygen	14.54	11.99	2.02	0.67	3.05	1.28	0.00	1.61
Ash	0.45	0.00	0.04	1.00	0.04	0.03	0.09	0.10

TABLE 3

"Short" Column Chromatography Analysis Results for Agglomerating Oils, wt%

	Phenol/ Tar Oil	Cresylic Acid	Mild Gas Tar	Used Motor Oil	V-161	V-178	V-1074	ROSE Resid
Aliphatics	0.99	1.15	13.30	61.5	32.2	21.31	19.2	3.44
Branched Aliphatics	5.45	0.85	1.13	1.58	1.29	3.10	0.48	0.80
Aromatics	12.60	1.33	31.16	23.9	33.85	58.17	65.6	76.5
Polars	80.96	96.67	54.41	12.9	32.64	17.42	13.8	19.2

TABLE 4

Proximate, Ultimate, and Heating Value Analyses for
Beulah Lignite and Spring Creek Subbituminous Coal

	Beulah	Spring Creek
Moisture, wt%	33.20	25.30
Proximate, mf, wt%		
Volatile Matter	46.08	44.54
Fixed Carbon	46.52	51.25
Ash	7.40	4.21
<u>Ultimate, mf, wt%</u>		
Carbon	64.18	71.39
Hydrogen	5.03	5.00
Nitrogen	0.70	0.99
Sulfur	1.10	0.29
Oxygen	21.57	18.10
Ash	7.40	4.21
Heating Value, mf, Btu/lb	10,960	12,390

The azeotropic moisture and Soxhlet-determined oil contents plus the air- and oven-drying losses of the agglomerates are presented for the three balance tests in Tables 5, 6, and 7. The analytically determined total carbon content and the calculated oil contents of the filtrates are presented in Table 8.

Moisture, oil, and solids balances were performed for each agglomeration test using one or more of the previously described balance methods. The range of raw agglomerate compositions and closures for the balance tests are presented in Table 9. Complete balances are presented in Appendix B.

The range of raw agglomerate compositions and balance closures indicates, in some instances, considerable variability among the different balance methods. Methods 3 and 4, which used oven-drying in conjunction with Soxhlet extraction, resulted in poor water and oil balance closures. The oil balance closure by these methods ranged from 85 to 92 wt% and the solids balance closure ranged from 117 to 127 wt% during the first Beulah agglomeration balance test. The poor closures were hypothesized to have resulted when some of the agglomerating oil polymerized during agglomerate oven-drying. Presumably the polymerized oils were inextractable by the methylene chloride during Soxhlet analysis causing an erroneously low raw agglomerate oil content. Balance Method 2, which did not use oven-drying in the agglomerate analysis scheme, resulted in more reasonable oil and solids balance closures of 102 and 105 wt%, respectively.

TABLE 5
Beulah Lignite Agglomerate Analysis
Balance Test 1, wt%

Agglomerate Type	Raw	Air-Dried	Oven-Dried Raw	Oven-Dried Air-Dried
Azeotropic Moisture	31.6	2.78	1.32	1.45
Soxhlet Oil	ND*	42.9	11.3	15.1
Air-Drying Loss	41.6	ND	ND	ND
Oven-Drying Loss	55.5	26.3	ND	ND

* Not determined.

TABLE 6
Beulah Lignite Agglomerate Analysis
Balance Test 2, wt%

Agglomerate Type	Raw	Air-Dried
Azeotropic Moisture	31.6	4.79
Soxhlet Oil	23.7	42.7
Air-Drying Loss	40.0	ND*

* Not determined.

TABLE 7
Spring Creek Subbituminous Agglomerate Analysis
Balance Test 1, wt%

Agglomerate Type	Raw	Air-Dried
Azeotropic Moisture	28.4	6.28
Soxhlet Oil	37.2	40.9
Air-Drying Loss	33.6	ND*

* Not determined.

TABLE 8
Agglomeration Filtrate Analysis
Beulah Lignite and Spring Creek Subbituminous Balance Tests

Balance Test	Beulah Test 1	Beulah Test 2	Spring Creek Test 1
Total Carbon Content, mg/L	12,800	8,770	9,440
Total Oil Content, mg/L	16,600	11,400	12,300

TABLE 9
Summary of Agglomeration Balance Tests
Beulah Lignite and Spring Creek Subbituminous, wt%

Balance Test	Beulah Test 1	Beulah Test 2	Spring Creek Test 1
Raw Agglomerate Composition			
Moisture	31.6	31.6	28.4
Oil	29.5 - 36.6	23.7 - 36.9	36.5 - 37.2
Solids	31.8 - 38.9	31.5 - 44.7	34.4 - 35.1
Balance Closure			
Moisture	99.0	97.9	99.1
Oil	85.2 - 102	70.1 - 100	89.6 - 90.7
Solids	105 - 117	105 - 150	102 - 104

Subsequent agglomeration tests with Beulah lignite and Spring Creek subbituminous used only Methods 1 and 2 to calculate raw agglomerate oil contents. The results with these two methods were not always consistent though Method 2 did tend to give the most reasonable oil and solids balance closures. The oil and solids balance closures with Method 2 for Beulah lignite were 100 and 105 wt%, respectively. Similarly, the oil and solids balance closures with Method 2 for Spring Creek subbituminous were 91 and 102 wt%, respectively.

Comparison of the balance calculation methods indicates that Methods 1 and 2 are preferred to Methods 3 and 4. The former methods require fewer analyses and calculations. Also, these methods avoid the potential for oil polymerization during oven-drying and the deleterious effect on oil content determination.

Based on the more reasonable balance test closures with Beulah lignite, approximately 83 to 87 wt% of the agglomerating oil added during the process is collected on the agglomerates and tailings. The balance of the oil, 14 to 17 wt%, remains solubilized in the process water. The oil in the process water and on the tailings would be recovered by recycling the process

water and the tailings to the agglomeration stage during continuous processing.

The raw Beulah lignite agglomerates were determined to lose approximately 31 to 32 wt% of their oil and 91 to 95 wt% of their moisture to evaporation during air-drying at room temperature. The evaporated oil and moisture would also be condensed and recycled for use in the agglomeration stage.

The single balance test with Spring Creek produced similar results with approximately 27 and 85 wt% of the oil and moisture evaporated during air-drying. Approximately 17 wt% of the agglomerating oil remained solubilized in the process water; the balance of the agglomerating oil was on the agglomerates and tailings.

5.0 OIL RECOVERY FROM PROCESS WATER BY SOLVENT EXTRACTION

Solvent extraction was evaluated as a method to recover, for recycle, soluble agglomerating oil from the agglomeration process water and to reduce the phenolics concentration to a level suitable for conventional biological wastewater treatment methods. Also, solvent extraction was tested as a method to verify the process water total oil content as calculated from the total carbon content.

5.1 Experimental Procedure

Solvent extraction was performed in a 2-L separatory funnel on 500 g of low-pH agglomeration process water using methylene chloride as the solvent. Prior to solvent extraction, the total soluble oil content of the process water was determined by the method described in Section 4.1. The acidic oil fractions (phenols, etc.) were eluted first using 50 mL of solvent, then the process water was neutralized with a dilute NaOH solution prior to extraction of polyaromatics (benzene, naphthalene, phenanthrene, etc.). The process water was then basified to allow extraction of basic nitrogen compounds (quinoline, aniline, etc.). The methylene chloride was evaporated from the eluted fractions to recover the acidic, neutral, and basic oil fractions. The total mass of extracted oil was then compared to the oil content calculated from the total carbon content.

5.2 Results and Discussion

Process water generated during an agglomeration test was analyzed to determine the concentration of organics resulting from solubilized agglomerating oil. The process water was analyzed to determine biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), total carbon (TC), total solids (TS), total suspended solids (TSS), and total phenolics (4). The results of the analysis are presented in Table 10.

The high COD to BOD ratio of 2.71:1 indicated that a significant level of refractory COD (+30,000 mg/L) would remain in the water, presuming biological treatment could remove +90% of the BOD. However, the exceedingly high phenolics content of almost 10,000 mg/L would probably prevent biological treatment of this water without prior reduction of phenolics by a pretreatment

TABLE 10
Process Water Analysis
Solvent-Recovery Testing

Constituent	Concentration, mg/L
BOD	17,700
COD	48,000
TOC	12,800
TC	16,500
TS	15,100
TSS	106
Phenolics	9,980

process. Consequently, solvent extraction was tested as an agglomeration process water pretreatment step.

Extraction of the process water with methylene chloride resulted in elution of 13.6 g of phenolic oils (acidic), 1.4 g of neutral oils, and 10.9 g of basic oils. The total extracted-oil concentration, based on 500 mL of process water, was approximately 51,500 mg/L. Comparatively, the total oil concentration, determined from the total carbon content, was approximately 21,400 mg/L, or 42% of that determined by solvent extraction. Similarly, the phenolic oil concentration determined by solvent extraction was 27,200 mg/L which compares to 9,980 mg/L as determined by standard water analysis techniques.

The oil concentration determined by solvent extraction was concluded to be inaccurate, probably due to inadequate evaporation of solvent during the solvent recovery process. Consequently, the solvent extraction technique has been temporarily dismissed as a method of determining oil content and recovering the oil for recycle.

6.0 OIL RECOVERY FROM PROCESS WATER BY ABSORPTION ON COAL

Raw and acid-cleaned coals, prepared for subsequent agglomeration tests, were investigated as an absorbant for recovering soluble oil from the agglomeration process water. This method was investigated as an alternative to solvent extraction for oil recovery and process water pretreatment. Presumably, the raw or acid-cleaned coal used to recover oil from the process water would be fed directly to the agglomeration step, thus reducing the quantity of makeup agglomerating oil in a continuous process.

6.1 Experimental Procedure

The raw or acid-cleaned -30-mesh Beulah lignite was added to 100 mL of process water and agitated using a T-bar mixer at approximately 800 rpm. Soluble oil absorption/desorption equilibria were assumed to be achieved within the 5-minute mixing period. The effect of coal quantity on oil removal was observed by varying the coal-to-process water ratio (g/mL). The "clean" process water was separated from the absorbent (raw or acid-cleaned coal) by

Buchner filtration. The "raw" and "clean" process waters were analyzed by Standard Methods 505A and 510C to determine total carbon and total phenolics content, respectively (4).

6.2 Results and Discussion

Process water generated in several different agglomeration experiments was treated using coal-to-water ratios in the range of 0.1 to 1.0 g/mL, and the effect on total carbon and total phenolics content is illustrated in Figures 2 and 3.

The acid-cleaned coal reduced the total carbon and total phenolics concentrations by 87 and 89 wt%, respectively, at a coal/water ratio of only 0.8. The raw coal was slightly less effective, absorbing 85% of the total carbon and 81% of the total phenolics at a coal/water ratio of 1.0 g/mL. At coal/water ratios as low as 0.25 to 0.50, the acid-cleaned and raw coals were able to reduce the total carbon concentration by 50% to 70%.

Preliminary testing indicated that approximately 90% of the soluble agglomerating oil could be recovered from the process water at coal/water ratios of around 1.0 g/mL. The level of removal would need to be enhanced because up to 2 wt% of the agglomerating oil added to the process still remains solubilized in the process water. This technique will be investigated further to determine the maximum level of total carbon and total phenolics reduction and the associated coal/water ratio.

7.0 AGGLOMERATE DEOILING

Thermal deoiling was investigated as a method for reducing the oil content of agglomerates and recovering the oil for recycle to the agglomeration stage. Thermal deoiling was also investigated as a method of producing a stronger, more stable lump fuel suitable for transport and resistant to moisture reabsorption and spontaneous combustion.

7.1 Experimental Procedure

Agglomeration deoiling tests were performed using two different systems, a 2-gallon batch reactor autoclave and a batch fluid-bed reactor. The two deoiling systems are illustrated in Figures 4 and 5.

The first deoiling system was an externally heated 2-gallon autoclave equipped with a single temperature controller and a single thermocouple to monitor agglomerate bed temperature. A test consisted of charging a 30-mesh basket with approximately 300 g of air-dried agglomerates and placing the basket into the room temperature autoclave. The heaters were activated after sealing the reactor, and an unheated nitrogen purge was introduced at the bottom of the autoclave to aid evacuation of the vaporized agglomerating oil and moisture. The agglomerates were maintained at temperature for 45 minutes, after which the reactor was allowed to cool before recovering the deoiled agglomerates. The vaporized agglomerating oils and moisture were recovered by water- and ice water-cooled condensers. The weights of the air-dried and deoiled agglomerates plus the condensables were recorded to determine the deoiling efficiency and material recovery.

Figure 2. Reduction of process water total carbon and total phenolics by absorption with acid-cleaned Beulah lignite.

Figure 3. Reduction of process water total carbon and total phenolics by absorption with raw Beulah lignite.

Figure 4. Batch autoclave thermal deoiling system.

Figure 5. Batch fluid-bed thermal deoiling system.

The second deoiling system was an externally heated batch fluid-bed reactor with an internal diameter of 1.5 in and a heated zone 9 in long. The agglomerates, determined from shakedown testing, were 100 g. Prior to charging the air-dried agglomerates, the fluid-bed reactor was preheated to the desired deoiling temperature using superheated steam. The external heaters were used to help maintain deoiling temperature. The air-dried agglomerates were charged to the preheated reactor from a pressurized hopper through a manually operated gate valve. Temperature monitoring and recording were provided at the reactor inlet; 2, 4, and 6 in above the distributor plate; and at the reactor outlet. A 100-mesh screen was installed at the reactor outlet to prevent entrainment of agglomerates or agglomerate fines. The agglomerates were treated for 40 minutes using superheated nitrogen or steam as the fluidizing and thermal deoiling medium. The vaporized agglomerating oil and moisture were recovered using two water-cooled condensers. The agglomerates were discharged from the pressurized reactor through a gate valve into a collection vessel. The weights of the air-dried and deoiled agglomerates and the condensables were recorded to determine the deoiling efficiency and material recovery.

7.2 Results and Discussion

7.2.1 Superheated-Nitrogen Deoiling Tests

A single deoiling test was performed using the batch autoclave deoiling system. Approximately 315 g of air-dried agglomerates were deoiled at a nominal temperature of 150°C for 1 hour. The deoiling test was considered a failure, however, for a number of reasons. First, temperature control was difficult and, over the test period, the agglomerate bed temperature increased to approximately 170°C. Second, the mass loss during the deoiling test was only 28 wt%, which is considerably less than evaporative loss by oven-drying at 105°C. Third, the mass balance closure was only 93.5 wt%, suggesting poor recovery of evaporated oil and moisture. As a consequence of these difficulties, the batch autoclave was temporarily abandoned as a thermal deoiling system, and subsequent deoiling tests were attempted with the batch fluid-bed reactor.

A series of four batch fluid-bed deoiling tests was performed at 200°C using superheated nitrogen as the deoiling and fluidizing medium. The deoiled agglomerates from the four tests were combined into a composite sample as was the condensed oil/moisture fractions. The fluid-bed reactor proved to be an ideal system for maintaining a proper and uniform bed temperature. The agitation induced by the fluidizing gas produced little agglomerate decrepitation or fines production. A total of 401 g of air-dried agglomerates were deoiled, producing 251 g of deoiled agglomerates and 117 g of condensed oil/moisture. The material balance closure was approximately 92 wt% with the loss attributed to poor recovery of evaporated oil and moisture.

The Soxhlet oil and azeotropic moisture contents of the air-dried and nitrogen-deoiled agglomerates are presented in Table 11. The air-dried agglomerate moisture and oil contents were 5.9 and 38 wt%, respectively, which compare to the deoiled agglomerate moisture and oil contents of 2.0 and 0.3 wt%, respectively. A moisture and oil balance, assuming 100% recovery of agglomerate solids, indicated that the agglomerate weight loss did not equal the oil and moisture weight losses. The Soxhlet oil content of the deoiled agglomerates was estimated to be low by 7.5 wt%, presumably due to the

TABLE 11

Beulah Lignite Agglomerate Moisture and Oil Contents
Superheated-Nitrogen and Steam-Deoiling Tests, wt%

Agglomerates	Air-Dried	Nitrogen Deoiled	Steam Deoiled
Azeotropic Moisture	5.85	2.04	2.47
Soxhlet Oil	37.7	0.33	0.24

hypothesized polymerization of agglomerating oil during the deoiling tests. It was not possible to verify this estimate however, because of the poor overall material balance closure.

The condensate from the nitrogen deoiling experiment was analyzed by open column chromatography to determine the concentration of aliphatics, aromatics, and polars. The concentrations of linear and small aliphatics, branched and large aliphatics, aromatics, and polars were determined to be 0.85, 1.31, 2.93, and 94.9 wt%, respectively. These concentrations compare to the original agglomerating oil compositions of 0.96, 5.29, 12.2, and 78.5 wt%, respectively. The apparent increase in the polar content may have been caused by one or more concurrent phenomena including preferential absorption of specific oil components during agglomeration, evaporation of specific oil components during deoiling, and the inefficient recovery of specific volatile oil components during deoiling. The recovery of vaporized oils and moisture would have to be greatly enhanced and the soluble oil in the process water would have to be isolated and analyzed to substantiate these suggestions.

Considering the relative simplicity, the uniform temperature control, and the minimal agglomerate degradation, fluid-bed deoiling with superheated nitrogen will be investigated further, using this or a larger batch system.

7.2.2 Superheated-Steam Deoiling Tests

Two batch fluid-bed deoiling tests were performed at 230°C using superheated steam as the deoiling and fluidizing medium. The deoiled agglomerates from the two tests were combined into a composite sample as were the condensed oil/moisture fractions. A total of 202 g of air-dried agglomerates were deoiled, producing 113 g of deoiled agglomerates. The material balance closure was low at 89 wt% and this was attributed to the inefficient condensation of agglomerating oil and superheated steam.

The analysis of the air-dried and superheated steam deoiled agglomerates are presented in Table 11. The azeotropic moisture content and Soxhlet oil content of the deoiled agglomerates were 2.5 and 0.2 wt%, respectively, which compare to the air-dried agglomerate moisture and oil contents of 5.9 and 38 wt%, respectively. The extremely low oil content suggests almost complete removal during deoiling. Presumably this could have been substantiated by determining the mass of oil in the condensate stream. This effort was confounded by poor condensate recovery and by the inability to determine the

condensate oil concentration. In addition to being solubilized in the condensate, the oil existed as discrete droplets. The oil droplets would not settle out during decantation, but adhered to the separatory funnel walls. Because of the dispersed oil droplets and the resulting non-homogeneity of the condensate, the standard technique of determining total carbon content was not applicable.

Owing to the difficulties in accurately determining the oil content of the condensate and to the necessity to superheat, condense, and then treat large quantities of water/condensate, superheated steam deoiling will be temporarily abandoned as an oil recovery method.

8.0 AGGLOMERATE STRENGTH AND STABILITY TESTING

Preliminary strength and stability tests for agglomerates included durability toward abrasion and resistance toward moisture reabsorption. Strength and stability testing are necessary to determine if the agglomerates can maintain their integrity during the rigors of transportation and storage. Ideally the strength and stability of the agglomerates would be correlated to the moisture and oil contents as determined by the previously described analysis techniques.

8.1 Experimental Procedure

The resistance to abrasion was determined at the relatively mild conditions achieved by continuous vibration on the screens of a Ro-Tap sieve apparatus. Prior to durability testing, the agglomerates were carefully screened, avoiding breakage, to determine the agglomerate size distribution. The sized agglomerates were placed on the top screen, and the Ro-Tap machine was operated for 10 minutes. The size distribution of the agglomerates after durability testing was compared to the original distribution to determine the abrasion loss.

The resistance to moisture reabsorption was determined using a modified ASTM D1412 equilibrium moisture procedure. The agglomerates were not water soaked prior to equilibrium moisture testing in order to avoid possible agglomerate decrepitation. The agglomerates were incubated at 30°C at 96%-97% relative humidity until the weight change was less than 0.1 g per day. The final moisture content of the incubated agglomerates was calculated from the weight loss/gain and the initial azeotropic moisture content. The moisture content at equilibrium was not determined by the traditional oven-drying weight loss method because of potential agglomerating oil evaporation.

8.2 Results and Discussion

Durability and moisture reabsorption tests were performed on air-dried and oven-dried (105°C) agglomerates. The azeotropic moisture and Soxhlet oil contents of the air- and oven-dried agglomerates are presented in Table 12. The size distributions of agglomerates after durability testing were compared to the original distributions and the results are presented in Figures 6 and 7. The test results indicated that the moderate abrasion conditions during Ro-Tap sieve testing did not significantly reduce the air- or oven-dried agglomerate size. The moisture and oil content appeared to have little

TABLE 12

Beulah Lignite Agglomerate Moisture and Oil Contents
Strength and Stability Tests, wt%

Agglomerate Type	Air-Dried	Oven-Dried
Azeotropic Moisture	6.0	1.0
Soxhlet Oil	44.0	14.3
Equilibrium Moisture	ND*	10.4

* Not determined.

effect on agglomerate strength as the air- and oven-dried agglomerates exhibited similar size degradation.

The equilibrium moisture content of the oven-dried agglomerates was approximately 10 wt% which compares to the original oven-dried moisture content of 1.0 wt% and a raw Beulah lignite equilibrium moisture content of 27 wt%. The calculation of the air-dried agglomerate equilibrium moisture content was confounded by the simultaneous evaporation of agglomerating oil.

Future agglomerate strength tests will include drop, tumble, and compressive load tests similar to those used on raw, pelletized, or briquetted coals. These tests will be performed after development of a reliable deoiling system which can process the required quantities of agglomerates.

9.0 ACID-CLEANING TESTS

The inorganics of the LRCs tested in the EERC agglomeration process are predominantly associated with the organic matrix as the carboxylic or phenolic salts of alkali and alkaline earth metals. Physical cleaning is only effective for removing extraneous minerals and has a limited effect on the removal of deposit-causing inorganic species such as sodium and calcium. Consequently, ion exchange via acid cleaning is necessary to remove these constituents and significantly lower the inorganic content. Added benefits of acid cleaning prior to agglomeration are the dissolution of acid-soluble extraneous minerals and the surface conditioning that enhances the effectiveness of the agglomerating oil to bind the coal. The acid is hypothesized to change the surface chemistry of the LRCs by reducing oleophobic sites.

Several experiments were performed using nitric acid leaching on Beulah lignite and Spring Creek subbituminous coal. The results from this testing helped determine the optimum conditions for achieving maximum ash reduction with these two coal samples. The acid-cleaning experiments were performed under the same conditions as those utilized prior to agglomeration.

Figure 6. Size distribution of air-dried agglomerates before and after Ro-Tap durability testing.

Figure 7. Size distribution of oven-dried agglomerates before and after Ro-Tap durability testing.

A titrimetric procedure using 0.1 N sodium hydroxide was developed to determine acid consumption as a function of acid solution strength and ash reduction.

Table 13 presents the results of cleaning Beulah lignite with nitric acid solutions of 0.12 to 1.29 M. Ash reductions ranged from 18 to 63 wt%, and the highest ash reductions were achieved when the acid concentration was greater than 0.5 M. At acid concentrations less than 0.5 M, the nitric acid is almost completely consumed.

Tables 14 and 15 present the results of cleaning Spring Creek subbituminous coal with nitric acid solutions of 0.14 to 0.89 and 0.16 to 1.28 M, respectively. Ash reductions in Table 14 ranged from 15 to 40 wt% and acid consumption ranged from 50 wt% at the highest concentration to 96 wt% at the lowest acid concentration. The acid cost from this testing produced results that range from \$4.29 to \$14.67 per ton coal. Ash reductions in Table 15 ranged from 27 to 47 wt% and acid consumption ranged from 35 to 97 wt%. Acid cost for this experiment ranged from \$5.07 to \$14.58 per ton of coal. The results from acid cleaning the coal presented in Table 15 indicate that the coal sample used in Table 14 was slightly oxidized. This was substantiated by the moisture analysis that indicated a moisture content for the Table 14 sample was 17 wt%. This is considerably lower than the moisture for the Table 15 sample that had a moisture content of 25 wt%, which is more typical for this coal. Oxidation of the coal surface inhibits the ability of the acid to ion-exchange with the coal, and the ash reduction is not as great for an oxidized sample.

Figures 8 and 9 indicate the effect of nitric acid cleaning on the ash constituents of Beulah lignite and Spring Creek subbituminous coal, respectively. For Beulah lignite, maximum removal of ion-exchangeable species is essentially achieved at a concentration of ~0.5 M. Sodium, although low in this coal sample, is nearly completely removed, and calcium and magnesium are reduced by ~82 wt% at these acid concentrations. At an acid concentration of 0.5 M, the acid cost per ton of coal cleaned, from Table 13, is approximately \$13, based on \$185/ton for 70 wt% concentrated nitric acid.

Spring Creek subbituminous coal results in Figure 9 indicate significant removal of ion-exchangeable species is essentially achieved at a concentration of 0.16 M. Reduction in sodium, magnesium and calcium content at this concentration is 81, 69 and 34 wt%, respectively. In comparison at 1.28 M these species are reduced in concentration by 95, 79 and 68 wt%, respectively. This comparison indicates that cost-effective cleaning of this coal could be achieved at 0.16 M. Since the ion-exchangeable species are significantly reduced at this concentration and the acid cost is approximately \$5.1/ton coal, based on \$185/ton for 70 wt% concentrated nitric acid, this should be the acid concentration of choice for achieving ion-exchangeable mineral reduction. If higher acid concentrations are chosen, it is apparent that substantial reduction of ion-exchangeable inorganics in LRCs is more costly. As with Beulah, acid cleaning of Spring Creek does not appreciably change the discrete mineral content.

The data presented indicate that Spring Creek acid cleaning is optimized at ~0.16 M, and for Beulah it is optimized at ~0.5 M. From the data in the tables and figures, it is apparent that substantial reduction of ion-exchangeable inorganics in LRCs is costly when using nitric acid.

TABLE 13

Nitric Acid-Cleaning Results for Beulah Lignite

Acid Molarity:	1.29	0.93	0.64	0.47	0.32	0.23	0.16	0.12
Ash Content ¹	2.84	3.08	2.91	3.47	4.25	5.43	5.70	6.26
Ash Reduction, wt%	63.4	60.2	63.1	54.7	44.1	29.8	23.6	18.6
Acid Consumption, wt%	41.5	51.6	63.3	84.0	95.0	98.6	99.1	99.6
<u>1b Conc. Acid</u> <u>100-1b Coal</u>	9.48	8.50	7.17	6.99	5.40	4.02	2.81	2.11
Acid Cost, \$/Ton Coal ²	17.54	15.73	13.26	12.93	9.99	7.43	5.19	3.91

¹ Raw coal ash content = 7.4 wt% mf.

² \$185/ton; 70 wt% concentrated nitric acid.

TABLE 14

Nitric Acid-Cleaning Results for Spring Creek Subbituminous Coal

Acid Molarity:	0.89	0.46	0.25	0.14
Ash Content ¹	2.93	3.28	3.61	4.17
Ash Reduction, wt%	40.2	34.5	27.7	15.0
Acid Consumption, wt%	50.2	66.8	88.6	95.6
<u>1b Conc. Acid</u> <u>100-1b Coal</u>	7.93	5.46	3.85	2.32
Acid Cost, \$/Ton Coal ²	14.67	10.10	7.12	4.29

¹ Raw coal ash content = 5.05 wt% mf.

² \$185/ton; 70 wt% concentrated nitric acid.

TABLE 15

Nitric Acid-Cleaning Results for Spring Creek Subbituminous Coal

Acid Molarity:	1.28	0.63	0.32	0.16
Ash Content ¹	2.24	2.53	2.76	3.20
Ash Reduction, wt%	46.9	41.2	35.7	26.9
Acid Consumption, wt%	34.8	44.2	70.3	96.6
<u>lb Conc. Acid</u> <u>100-lb Coal</u>	7.88	4.96	3.99	2.74
Acid Cost, \$/Ton Coal ²	14.58	9.18	7.38	5.07

¹ Raw coal ash content = 4.37 wt% mf.

² \$185/ton; 70 wt% concentrated nitric acid.

Figure 8. Mass of ash constituents for raw coal and nitric acid-cleaned fractions of Beulah lignite.

Figure 9. Mass of ash constituents for raw coal and nitric acid-cleaned fractions of Spring Creek subbituminous coal.

In addition to nitric acid cleaning, acid cleaning was performed on these two coals using a solution of carbonic acid. The carbonic acid source was carbonated sparkling water. The acid only slightly reduced the ash content of Beulah (7.87 compared to 7.43) and has essentially no effect on the ash content of Spring Creek (3.92 compared to 3.76). Although this acid did not appear to be effective, an ash analysis should be performed to see if any ion-exchange was achieved with the sodium in the coals.

In order to utilize acid cleaning in the agglomeration process, methods have to be developed to either recycle the acid or neutralize it with a basic solution. Sodium hydroxide would be very costly to use for neutralization; therefore, testing was initiated using hydrated lime as a neutralizing agent. Initially the filtrate was neutralized using hydrated lime powder. This was not successful because an endpoint was difficult to observe since the hydrated lime did not readily go into solution. Therefore, a solution of 1 M hydrated lime was made for addition to filtrate solutions. The target pH was 7.0; however, attainment of a pH very near 7.0 was difficult to achieve, especially at low initial residual acid concentrations. Experiments with filtrates from the higher acid filtrates indicated that approximately 1 mole of hydrated lime is required to neutralize 2 moles of acid. For example, 30 mL of 0.31 M filtrate solution required 5 mL of 1.0 M hydrated lime solution to raise the pH to 7.89.

Further testing needs to be performed using the hydrated lime solution in order to better establish the conditions necessary to neutralize the filtrate.

10.0 COLLOIDAL COAL CLEANING

Colloidal coal cleaning was investigated as a method to reduce the ash content of LRC by separating the carbonaceous coal material from the inorganics. Extraction of a LRC with an alkaline medium can produce a colloidal humate dispersion or a hydrosol from which the humic acid can be precipitated (7) resulting in low-ash fuel suitable for advanced combustion systems.

10.1 Experimental Procedure

Approximately 50 g of coal was added to 250 g of a 10 wt% NaOH solution, and the mixture was blended at 11,000 rpm for 60 minutes using a Virtis high-shear homogenizer. The blended slurry was centrifuged at 3600 rpm for 30 minutes using an IEC Model K centrifuge to separate the supernatant hydrosol from the extracted coal residue. The humic acid was precipitated by adding concentrated nitric acid to the hydrosol until the pH was slightly below 1. The humic acid was recovered by centrifugation at 3600 rpm for 30 minutes. The residue and humic acid were analyzed by standard methods to determine ash and moisture contents. The weights of the residue, humic acid, wash water, and centrate were recorded for determination of ash reduction and material recovery.

10.2 Results and Discussion

A preliminary colloidal coal-cleaning test was performed using pulverized Beulah lignite in order to become familiar with the process. The products from colloidal coal cleaning of the Beulah lignite were a dark residue, presumably containing unextracted coal and coal inorganics, plus the brown, low-density, semifluid humic acid which was devoid of distinct particles. The acidified process water was essentially clear, indicating that hydrosol had been completely precipitated as humic acid.

Approximately 188 g of residue containing 12.3 wt% solids and approximately 49 g of humic acid containing 13.6 wt% solids were recovered from 50 g (33 g solids) of coal. The residue and humic acid ash contents were 50.7 and 22.2 wt%, respectively, on a moisture-free basis. The high combustible content of the residue suggests that a considerable quantity of coal solids remained unextracted. This may have resulted from insufficient mixing time, improper coal size, or a low NaOH/coal ratio. Contrastingly, the high ash content of the humic acid suggests that the precipitate contained a considerable quantity of the sodium humate. Previous colloidal coal-cleaning tests have indicated the necessity for numerous washings with water to reduce the ash (Na^+) content (7).

Additional colloidal coal-cleaning tests will be performed with Beulah lignite to determine the NaOH/coal ratio required to optimize coal inorganic reduction and material recovery. The number of water washings required to achieve the minimum humic acid ash content will also be determined. The process will also be modified to eliminate the acidification step by precipitating a calcium humate instead of humic acid. The calcium humate could be fired in conventional or advanced combustion systems with high sulfur coals so that the atomically dispersed calcium can act as a sulfur oxide sorbent.

11.0 CONCLUSIONS

1. Agglomeration process scale-up was successful using a 20-liter pail to form larger quantities of agglomerates for analysis.
2. Ash reductions of greater than 50 wt% for Beulah lignite were achieved when the acid concentration was ~ 0.5 M.
3. Ash reductions for Spring Creek subbituminous coal ranged from 15 to 47 wt% for acid concentrations from 0.14 to 1.28 M.
4. Significant removal of ion-exchangeable species for Beulah lignite using nitric acid is essentially achieved at ~ 0.5 M, and for Spring Creek subbituminous coal it is achieved at ~ 0.16 M.
5. The most effective oils in the EERC agglomeration process have high oxygen and polar contents.
6. Liquefaction oils and used crankcase oil are only effective in oil agglomeration using high-shear conditions or surfactant addition prior to low-shear mixing conditions.
7. Agglomeration was successful when sources of ionic strength were potassium nitrate, calcium acetate, and carbonic acid.
8. Agglomeration can be achieved without surface conditioning or ion-exchange prior to agglomeration.
9. Methods of analysis have been investigated that produce material balances ranging from 91% to 105%.
10. Oil remaining solubilized in the process water following agglomeration ranges from 14% to 17%.
11. Solvent extraction methods are not acceptable for recovering oil from process water, due to inadequate evaporation of solvent during the solvent recovery process.
12. Agglomerant can be recovered from process water using raw or acid-cleaned coal to absorb the solubilized agglomerant with recoveries ranging from 81% to 89%.
13. Oxygen and polar content of agglomerants could be used to screen candidates for LRC agglomeration.
14. Autoclave deoiling has proven to be an ineffective method for agglomerate deoiling due to the poor recovery of material and inadequate temperature control of the system.
15. Fluidized-bed deoiling is an effective method for deoiling the agglomerates using superheated nitrogen as the deoiling and fluidizing medium because of its simplicity, uniform temperature control, and minimal agglomerate degradation.

16. Fluidized-bed deoiling using superheated steam is an inadequate deoiling method because of poor condensate recovery and difficulty in accurately determining oil content of the condensate.
17. Residue and humic acid ash contents following colloidal coal cleaning were 50.7 and 22.2 wt%, respectively, indicating that additional extraction on the residue and additional washing of the humic acid may be needed.
18. Air- and oven-dried agglomerates are able to withstand moderate Ro-Tap abrasion testing with minimal size degradation.
19. Equilibrium moisture contents of oven-dried agglomerates are approximately 10 wt% compared to 27 wt% for raw Beulah coal.

12.0 FUTURE RESEARCH EFFORTS

Testing for the next year will concentrate on improving the fluid-bed thermal deoiling system to achieve near 100% balance closure. Sufficient deoiling tests will be performed to provide agglomerates for strength and stability testing. The strength and stability of the deoiled agglomerates will be correlated to the analytically determined moisture and oil contents. Successful investigation of these tasks will determine if a transportable solid fuel can be produced and whether deoiling is necessary to produce a transportable fuel. A plant design and economic analysis will be prepared based on the consumption of acid and agglomerating oil.

1. Agglomeration design scale-up of recovery processes have to be optimized in order to eliminate labor-intensive steps that result in loss of product.
2. Further investigation of ion-exchange using carbonic acid is needed for comparison with nitric acid for removal of ion-exchangeable species.
3. Analysis for trace metals in used crankcase oil should be performed if this oil is chosen as an agglomerant.
4. Perform ash fusion analysis on agglomerates that are ion-exchanged with nitric and carbonic acid and on those that are not ion-exchanged and determine which has the most promising combustion properties.
5. Do further analysis on neutralizing filtrate using hydrated lime, and determine the feasibility of its use in the agglomeration process versus the reuse of the acid.

13.0 REFERENCES

1. Malterer, T.J. et al. "Screening of Low-Rank Coals for Low-Ash Fuel Preparation," In Proceedings of the 13th International Conference on Coal and Slurry Technology; Denver, CO, April 1988, pp 443-457.

2. Potas, T.A. et al. "Continuous Production of Deep-Cleaned Low-Rank Coal," In Proceedings of the 14th International Conference on Coal and Slurry Technology; Clearwater, FL, April 1989, pp 593-602.
3. Smit, F.J.; Maas, D.J. "Preparation and Analyses of Low-Rank Coals for Combustion Applications," final report; DE-AC18-84FC10623, U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, WV, October 1986.
4. Greenber, A.E.; Trussell, R.R.; Clesceri, L.S., Eds. Standard Methods for the Examination of Water and Wastewater; 16th Ed.; Washington, D.C.: American Public Health Association, 1985.
5. Southern Company Services, Inc. "Engineering Development of Selective Agglomeration: Task 6: Operation of the Component Development Test Facility," U.S. Department of Energy Contract No. DE-AC22-89PC88879, September 1991.
6. Musich, M.A. et al. "Beneficiation of Low-Rank Coals," Semiannual Technical Progress Report for the Period July 1, 1991, through December 31, 1991; U.S. Department of Energy, Pittsburgh Energy Technology Center, January 1992.
7. Olson, E.S.; Diehl, J.W.; Froehlich, M.L. "Hydrosols from Low-Rank Coals: 1. Preparation and Properties," FUEL 67, 1053-1061.

APPENDIX A

Sequence to Determine Moisture and Oil Contents of Raw Agglomerates

Appendix A

APPENDIX B

Moisture, Oil, and Solids Balances

TABLE B-1
Beulah Agglomeration Balance Test 1
Raw Agglomerate Oil Calculation Method 2

Component	HNO ₃	Water	Oil	Solids	Total
Influents, g					
Coal	0.0	61.0	0.0	139.0	200.0
Acid Solution	12.0	388.0	0.0	0.0	400.0
Agglomerant	0.0	10.8	189.3	0.0	200.1
<u>Wash/Rinse Water</u>	<u>0.0</u>	<u>1308.8</u>	<u>0.0</u>	<u>0.0</u>	<u>1308.8</u>
Total	12.0	1768.6	189.3	139.0	2108.9
Effluents, g					
Raw Agglomerates	0.0	129.0	149.5	129.8	408.3
Raw Tailings	0.0	14.5	16.0	15.4	45.9
<u>Filtrate/Rinse Water</u>	<u>12.0</u>	<u>1607.9</u>	<u>27.2</u>	<u>0.0</u>	<u>1647.1</u>
Total	12.0	1751.4	192.7	145.2	2101.3
Closure, wt%	100.0	99.0	101.8	104.5	99.6

TABLE B-2
Beulah Agglomeration Balance Test 1
Raw Agglomerate Oil Calculation Method 3

Component	HNO ₃	Water	Oil	Solids	Total
Influents, g					
Coal	0.0	61.0	0.0	139.0	200.0
Acid Solution	12.0	388.0	0.0	0.0	400.0
Agglomerant	0.0	10.8	189.3	0.0	200.1
<u>Wash/Rinse Water</u>	<u>0.0</u>	<u>1308.8</u>	<u>0.0</u>	<u>0.0</u>	<u>1308.8</u>
Total	12.0	1768.6	189.3	139.0	2108.9
Effluents, g					
Raw Agglomerates	0.0	129.0	120.4	158.9	408.3
Raw Tailings	0.0	14.5	13.5	17.9	45.9
<u>Filtrate/Rinse Water</u>	<u>12.0</u>	<u>1607.9</u>	<u>27.2</u>	<u>0.0</u>	<u>1647.1</u>
Total	12.0	1751.4	161.1	176.8	2101.3
Closure, wt%	100.0	99.0	85.1	127.2	99.6

TABLE B-3
Beulah Agglomeration Balance Test 1
Raw Agglomerate Oil Calculation Method 4

Component	HNO ₃	Water	Oil	Solids	Total
Influents, g					
Coal	0.0	61.0	0.0	139.0	200.0
Acid Solution	12.0	388.0	0.0	0.0	400.0
Agglomerant	0.0	10.8	189.3	0.0	200.1
Wash/Rinse Water	<u>0.0</u>	<u>1308.8</u>	<u>0.0</u>	<u>0.0</u>	<u>1308.8</u>
Total	12.0	1768.6	189.3	139.0	2108.9
Effluents, g					
Raw Agglomerates	0.0	129.0	132.7	146.6	408.3
Raw Tailings	0.0	14.5	14.9	16.5	45.9
Filtrate/Rinse Water	<u>12.0</u>	<u>1607.9</u>	<u>27.2</u>	<u>0.0</u>	<u>1647.1</u>
Total	12.0	1751.4	174.8	163.1	2101.3
Closure, wt%	100.0	99.0	92.3	117.3	99.6

TABLE B-4
Beulah Agglomeration Balance Test 2
Raw Agglomerate Oil Calculation Method 1

Component	HNO ₃	Water	Oil	Solids	Total
Influents, g					
Coal	0.0	34.1	0.0	65.9	100.0
Acid	8.6	192.0	0.0	0.0	200.6
Agglomerant	0.0	5.7	100.2	0.0	105.9
Wash/Rinse Water	<u>0.0</u>	<u>1364.1</u>	<u>0.0</u>	<u>0.0</u>	<u>1364.1</u>
Total	8.6	1595.9	100.2	65.9	1770.6
Effluents, g					
Raw Agglomerates	0.0	64.6	48.4	91.3	204.3
Raw Tailings	0.0	5.9	4.5	8.4	18.8
Filtrate	8.6	362.9	7.4	0.0	378.9
Rinse Water	<u>0.0</u>	<u>1129.7</u>	<u>9.9</u>	<u>0.0</u>	<u>1139.6</u>
Total	8.6	1563.1	70.2	99.7	1741.6
Closure, wt%	100.0	97.9	70.1	151.3	98.4

TABLE B-5
Beulah Agglomeration Balance Test 2
Raw Agglomerate Oil Calculation Method 2

Component	HNO ₃	Water	Oil	Solids	Total
Influents, g					
Coal	0.0	34.1	0.0	65.9	100.0
Acid	8.6	192.0	0.0	0.0	200.6
Agglomerant	0.0	5.7	100.2	0.0	105.9
<u>Wash/Rinse Water</u>	<u>0.0</u>	<u>1364.1</u>	<u>0.0</u>	<u>0.0</u>	<u>1364.1</u>
Total	8.6	1595.9	100.2	65.9	1770.6
Effluents, g					
Raw Agglomerates	0.0	64.6	75.4	64.3	204.3
Raw Tailings	0.0	5.9	7.8	5.1	18.8
Filtrate	8.6	362.9	7.4	0.0	378.9
<u>Rinse Water</u>	<u>0.0</u>	<u>1129.7</u>	<u>9.9</u>	<u>0.0</u>	<u>1139.6</u>
Total	8.6	1563.1	100.5	69.4	1741.6
Closure, wt%	100.0	97.9	100.3	105.3	98.4

TABLE B-6
Spring Creek Agglomeration Balance Test 1
Raw Agglomerate Oil Calculation Method 1

Component	HNO ₃	Water	Oil	Solids	Total
Influents, g					
Coal	0.0	24.6	0.0	75.4	100.0
Acid Solution	16.7	190.5	0.0	0.0	207.2
Agglomerant	0.0	5.7	100.5	0.0	106.2
<u>Wash/Rinse Water</u>	<u>0.0</u>	<u>1195.5</u>	<u>0.0</u>	<u>0.0</u>	<u>1195.5</u>
Total	16.7	1416.3	100.5	75.4	1608.9
Effluents, g					
Raw Agglomerates	0.0	51.9	68.0	63.0	182.9
Raw Tailings	0.0	6.1	6.3	14.0	26.4
<u>Filtrate/Rinse Water</u>	<u>16.7</u>	<u>1345.6</u>	<u>16.9</u>	<u>0.0</u>	<u>1379.2</u>
Total	16.7	1403.6	91.2	77.0	1588.5
Closure, wt%	100.0	99.1	90.7	102.1	98.7

TABLE B-7
Spring Creek Agglomeration Balance Test 1
Raw Agglomerate Oil Calculation Method 2

Component	HNO ₃	Water	Oil	Solids	Total
Influents, g					
Coal	0.0	24.6	0.0	75.4	100.0
Acid Solution	16.7	190.5	0.0	0.0	207.2
Agglomerant	0.0	5.7	100.5	0.0	106.2
Wash/Rinse Water	0.0	<u>1195.5</u>	<u>0.0</u>	<u>0.0</u>	<u>1195.5</u>
Total	16.7	1416.3	100.5	75.4	1608.9
Effluents, g					
Raw Agglomerates	0.0	51.9	66.8	64.2	182.9
Raw Tailings	0.0	6.1	6.3	14.0	26.4
Filtrate/Rinse Water	<u>16.7</u>	<u>1345.6</u>	<u>16.9</u>	<u>0.0</u>	<u>1379.2</u>
Total	16.7	1403.6	90.0	78.2	1588.5
Closure, wt%	100.0	99.1	89.6	103.7	98.7

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Beneficiation of Low-Rank Coal (4.2)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-88
		6. Completion Date 9-30-92

7. FY 91/92	8. Months or Quarters	1991						1992								
		JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN			
9. Cost Status		a. Dollars Expressed in Thousands						b. Dollar Scale								
10. Cost Chart																
Fund Source		Quarter				Cum. to Date	Tot Plan									
		1st	2nd	3rd	4th											
DOE	P	68	69	69	69	275	275									
	A	78	51	56	75	258										
	P															
	A															
	P															
	A															
	P															
	A															
	P															
	A															
Total P		68	69	69	69	275	275									
Total A		78	51	56	75	258										
Variance		(8)	18	13	(8)	17										
		P = Planned A = Actual						c. Cumulative Accrued Costs								
Total Planned Costs for Program/Project		Planned						Actual						Variance		
\$275																
		88						137						208		275
		78						127						183		258
		(8)						10						23		17

[illegible]

12. Remarks

13. Signature of Recipient and Date Rasmussen DeWalt 7/30/92	14. Signature of DOE Reviewing Representative and Date
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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Beneficiation of Low-Rank Coals (4.2)		3. Reporting Period 1-1-92 through 3-31-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 6-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Oil Agglomeration:				
a.1	Agglomeration with polar oil and carrier solvent	9-30-91	9-30-91		
a.2	Recycle and makeup requirements	12-31-91	1-31-92		
a.3	Process modifications	2-29-92	4-15-92		
a.4	Mass agglomerate formation and deoiling techniques	4-30-92			
a.5	Development of agglomerate stability analysis techniques	6-30-92			
Task B	Additional Cleaning Techniques:				
b.1	Froth flotation	8-31-91			
b.2	Colloidal coal cleaning	5-31-92			
Task C	Reports and Briefings--Final Report	7-31-92			

4.6 Nitrous Oxide Emissions

NITROUS OXIDE EMISSIONS

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

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NITROUS OXIDE EMISSIONS

1.0 BACKGROUND

Due to growing scientific and public concern relating elevated CO_2 concentration to changes in the global climate, other trace gases including CH_4 , chlorofluorocarbons (CFCs), and nitrous oxide (N_2O) have become suspect as contributors to the greenhouse effect and ozone depletion. N_2O is reportedly increasing in atmospheric concentrations at an estimated rate of 0.7 ppb per year (1) and was measured (1988) as present in the atmosphere at a concentration of 307 ppb (2).

Although the atmospheric concentrations of N_2O are low (1100 times less than CO_2), the relative strength of N_2O as an infrared absorber is reportedly 200 times more than CO_2 (2). In addition, N_2O , a stable compound, is transported to the stratosphere where it is photochemically oxidized to nitric oxide (NO), the major contributor to catalytic ozone depletion. The association and/or contribution of N_2O to the greenhouse effect and ozone reduction has led to considerable interest in determining the natural and man-made pathways to its formation and destruction.

The reported increase in atmospheric N_2O concentration over the last decade has prompted researchers to direct their attention toward anthropogenic sources of N_2O formation. These include biomass burning, fertilization, groundwater release through irrigation, and fossil fuel combustion. Pulverized coal combustion was first implicated as a major producer of N_2O emissions as a result of a sampling artifact. However, the established N_2O levels currently reported are typically less than 10 ppm, resulting in a negligible atmospheric contribution with respect to natural sources (1).

At present, attention has been focused upon advanced coal-combustion techniques currently becoming commercialized by the electric utilities industry. The most prominent of these are the fluidized-bed combustors (FBCs) and their variations (circulating, pressurized, or both). The main driving forces behind the use of fluidized-bed combustion have primarily been environmental concerns, fuel flexibility, and compatibility with low-cost fuels.

The role of the present project at the Energy and Environmental Research Center (EERC) is to determine the amount of atmospheric N_2O derived from coal combustion in FBCs. Additionally, the goal is to establish a comprehensive engineering model to assist in the prediction of N_2O emissions based upon operating and design considerations.

2.0 THREE-YEAR PROJECT OBJECTIVES

2.1 Task 1--Literature Survey

A literature survey will be performed to assess the current state of knowledge in the following areas: N_2O field measurements, measurement techniques, kinetics and reactions, and production of N_2O in FBC systems. Based on available information, an initial global model that predicts the formation of N_2O in FBC systems will be developed. Process variables to

consider should include temperature, pressure, reactant types and concentrations, and residence time effects.

2.2 Task 2--Equipment Design and Test Plan Development

A detailed test plan will be developed based on the results of Task 1. The plan shall include, but not be limited to, the following: design of the experimental facility, the experimental facility operating characteristics, experimental operating procedures, required instrumentation, and planned model development.

The facility will, at a minimum, have the following capabilities: suitability for determining N_2O reactions and reaction rates; bubbling, circulating, and transport regimes; variable temperature up to 1800°F, variable pressure up to 20 atm (300 psi), and variable velocity up to 20 fps; and the required instrumentation for diagnostics and data acquisition.

Parameters will be measured to provide data to determine the reaction kinetics and should include the mass-flow rate of reactants and products, the physical and chemical composition of reactant products, and the reaction temperature and pressure.

Parametric testing will be planned that will include comprehensive testing on one coal and sorbent, testing on two additional coals to look at the effect of fuel-bound nitrogen, and testing on one additional sorbent for the effect of magnesium.

2.3 Task 3--Facility Modification

The goal of this task is to construct a new reactor facility, or modify an existing facility, in accordance with the design approved by the Technical Monitor (TM) in Task 2.

2.4 Task 4--Experiments and Theory Development

The goal of this task is to perform the experimentation in accordance with the approved test plan developed in Task 2. Using this information, the global model, initiated in Task 1 to estimate the rates of N_2O reactions under FBC conditions, will be refined. The ultimate goal is to produce a simple global model for boiler designers to predict N_2O stack emissions and destruction in FBC systems.

2.5 Task 5--Analysis of Results and Final Report

The goal of Task 5 is to produce a final report which includes the following: reduced data for each test condition; parametric analysis and interpretation of data; a predictive model as a simple equation, otherwise as a compressed graphical representation and tabulations; and the original data in suitable format, i.e., a Lotus® spreadsheet.

2.6 Task 6--Protocol for Field Monitoring (Optional Task)

The EERC will proceed with work under Task 6 only after receiving written direction from the TM. The goal of this task is to develop a protocol for field monitoring. This will include the sampling plan, sampling

locations, test conditions, process monitoring, and the duration of the test. Sites for testing will be identified, with consideration given to the physical plant layout, access to sampling locations, combustor type, feasibility to site access, and operational parameters. The willingness of the boiler operator to participate in the sampling and allow release of the data must also be considered. The cost of each site visit will also be determined. The sampling protocol will be submitted to the Morgantown Energy Technology Center (METC) TM for approval before any sampling begins.

2.7 Task 7--Field Monitoring of N_2O Emissions (Optional Task)

EERC will proceed with work under Task 7 only after receiving written direction from the TM. The goal of this task is to perform field monitoring in accordance with the sampling protocol established in Task 6.

3.0 RESULTS FROM CIRCULATING FLUIDIZED-BED COMBUSTOR TESTING AT THE EERC

Testing was continued using the 1-MW_{th} circulating fluidized-bed combustor (CFBC) to assess the effect of operating parameters and fuel specifications on N_2O emissions. A schematic of the combustor and ancillary equipment is shown in Figure 1. The main combustor has an internal diameter of 0.5 m and is 12.5 m tall. It is refractory-lined and has heat exchange panels located throughout the combustor to control heat removal. A cyclone is used to collect and recirculate solids through an external heat exchanger that is combined with the loop seal. A detailed description of the unit and operating procedures can be found elsewhere (3).

Figure 1. Schematic of the 1-MW EERC pilot-scale CFBC.

Since the last reporting period, two additional coals, a New Mexico bituminous and a second Wyoming subbituminous, were fired in the pilot-scale CFBC. These combustion tests were performed under private contracts; therefore, the data were limited to studying the effects of operating temperature and coal rank. The data from these additional coals will be summarized and presented against the trends established with previously reported data.

The proximate, ultimate, and heating value analyses are shown in Table 1 for the complete database of seven coals. Coal ash analyses for these coals are presented in Table 2. The last two coals added to the database (Powder River subbituminous and New Mexico bituminous) have no notable differences in ash composition when compared to the other coals of similar rank. The Powder River Basin coal exhibited the typical high-calcium ash associated with these coals. The partitioning of the coal-nitrogen into the volatile matter and the char is also presented in Table 1. The distribution of the fuel-nitrogen into the char and volatile matter was determined by performing ultimate analyses on coal and coal-derived chars produced using ASTM (D3175) procedures for determining volatile matter. The quantity of nitrogen in the volatile matter was thus determined by difference. In this ASTM procedure, dried coal samples are heated for 7 min at a temperature of 1225 K in crucibles covered with lids.

The significance of the distribution of nitrogen in the coal is related to the reaction pathway in which fuel-bound nitrogen is converted to N_2O . The nonmatrix-bound nitrogen released with the volatile matter is free to react early in the combustion process through homogeneous or heterogeneous reaction pathways to form nitrogen or nitrogen oxides (NO , NO_2 , N_2O). In the case of CFB combustion, matrix-bound char nitrogen will produce nitrogen oxides through heterogeneous oxidation reactions throughout the combustor, but is believed to be a minor contributor to N_2O formation. The char nitrogen may also be gasified and react through homogeneous mechanisms.

3.1 Effect of Operating Parameters on N_2O Emissions from CFBC

The effects of CFBC operating parameters on N_2O emissions are shown in Figures 2 through 5. These parameters include temperature, excess air, sorbent-feed rate, and air staging. The N_2O emissions data in these figures are expressed on a $mg\ N_2O/MJ$ heat input basis. This effectively normalizes for fuel or nitrogen input rate as well as the combustor firing rate. Other bases, such as conversion of fuel nitrogen to N_2O or $ppm\ N_2O$ at 3% O_2 , assume a constant firing rate between tests as well as coals. Since firing rate can fluctuate with coals having high ash or moisture levels, we feel the firing rate basis will produce less error over the wide range of experimental conditions.

3.1.1 Effect of Temperature and Coal Rank

The effect of temperature and coal rank on N_2O emissions is presented in Figure 2. The pilot-scale results show appreciably different N_2O emissions for the seven coals tested. For a given temperature, the N_2O emissions were greatest for the higher-ranked New Mexico bituminous coal and the least for

TABLE 1

Analysis of Coals Tested in EERC 1-MW CFBC

Coal: Rank: Location:	Salt Creek HVC Bit Colorado	Blacksville HVA Bit Pennsylvania	Black Thunder Sub C Wyoming	Center Lignite N. Dakota	Asian Lignite Asia	New Mexico HVA Bit New Mexico	Powder River Sub C Wyoming
Proximate Analysis, as-received wt%							
Moisture	7.6	2.4	27.6	37.3	17.0	2.1	29.9
Volatile Matter (VM)	31.0	36.4	33.2	28.8	37.4	33.0	32.6
Fixed Carbon (FC)	42.7	52.9	34.6	28.8	7.6	52.5	33.0
Ash	18.6	8.5	4.6	5.1	38.0	12.4	4.5
FC/VM Ratio	1.38	1.45	1.04	1.00	0.20	1.59	1.01
Ultimate Analysis, as-received wt%							
Carbon	58.8	74.5	49.8	41.0	25.0	73.7	48.8
Hydrogen	5.0	5.2	6.6	7.0	4.2	4.9	6.7
Nitrogen	1.2	1.4	0.6	0.5	0.6	1.4	0.7
Sulfur	0.5	2.5	0.3	0.6	6.0	0.5	0.4
Oxygen	16.0	8.0	38.0	45.7	26.1	7.0	39.0
Ash	18.6	8.5	4.6	5.1	38.0	12.4	4.5
Nitrogen Distribution, ¹ % of total N							
Volatile Matter	43	36	27	25	88	36	31
Char	57	64	73	75	12	64	69
Higher Heating Value, as-received MJ/kg							
	23.85	30.94	20.08	16.25	10.90	30.09	19.66

¹ Nitrogen was measured in coal and in char prepared per ASTM proximate analysis. Nitrogen in volatile matter was determined by difference.

Note: All proximate, ultimate, and heating values are a result of averaging several samples for each coal.

TABLE 2

Analysis of Ash From Coals Tested in EERC 1-MW CFBC

Coal: Rank: Location:	Asian Lignite A Asia	Center Lignite A N. Dakota	Black Thunder Sub. C Wyoming	Salt Creek HVC Bit. Colorado	Blacksville HVA Bit. Pennsylvania	Powder River Sub. C Wyoming	New Mexico HVA Bit. New Mexico
Ash Composition, wt% of ash as oxides							
Silica, SiO ₂	31.8	14.8	28.5	59.9	43.7	31.5	48.6
Aluminum, Al ₂ O ₃	12.8	9.0	16.4	30.9	22.9	14.9	24.7
Ferric, Fe ₂ O ₃	13.5	14.2	6.4	3.0	16.8	5.4	6.4
Titanium, TiO ₂	0.2	0.4	1.4	1.1	0.7	1.2	0.9
Phosphorus, P ₂ O ₅	0.5	0.8	1.3	0.4	0.4	1.2	1.8
Calcium, CaO	18.6	22.4	24.3	1.5	5.4	25.3	8.5
Magnesium, MgO	3.3	9.6	7.9	1.5	1.2	7.1	2.0
Sodium, Na ₂ O	0.3	5.2	0.5	0.2	0.7	1.2	0.8
Potassium, K ₂ O	1.2	0.5	0.9	1.0	1.5	0.3	0.5
Sulfur, SO ₃	17.5	22.1	12.4	1.0	6.5	13.1	5.8
Ash Composition, wt% of coal as oxides							
Silica, SiO ₂	12.1	0.8	1.3	11.1	3.7	1.4	6.0
Aluminum, Al ₂ O ₃	4.9	0.5	0.8	5.7	1.9	0.7	3.1
Ferric, Fe ₂ O ₃	5.1	0.7	0.3	0.6	1.4	0.2	0.8
Titanium, TiO ₂	0.1	0.0	0.1	0.2	0.1	0.1	0.1
Phosphorus, P ₂ O ₅	0.2	0.0	0.1	0.1	0.0	0.1	0.2
Calcium, CaO	7.1	1.1	1.1	0.3	0.5	1.1	1.1
Magnesium, MgO	1.3	0.5	0.4	0.3	0.1	0.3	0.2
Sodium, Na ₂ O	0.1	0.3	0.0	0.0	0.1	0.1	0.1
Potassium, K ₂ O	0.5	0.0	0.0	0.2	0.1	0.0	0.1
Sulfur, SO ₃	6.7	1.1	0.0	0.2	0.6	0.6	0.7

the Powder River subbituminous coal. Two obvious temperature trends appear to be intimately related to coal rank. The first is that the absolute N_2O emissions from the higher-ranked bituminous coals are greater than from the lower-ranked coals. The second trend indicates that the temperature dependence (slope of temperature versus emissions curve) of a given coal rank is of similar magnitude. The latter trend probably corresponds to differences in coal composition or physical characteristics loosely associated with rank. As seen in Figure 2, the bituminous, lignite, and subbituminous coals have distinctly different slopes.

Further examination of Figure 2 shows that the effect of coal rank on N_2O emissions is not a continuous relation. At lower CFBC operating temperatures (<1120 K), bituminous coals yielded the highest N_2O emissions, followed by the lignites and then the subbituminous coals. It is also interesting to note that the temperature dependence of the lower-ranked lignite coals falls in a range between the higher-ranked bituminous and subbituminous coals. These results imply that either the chemistry of these subbituminous coals is unique, or that the coal-rank classifications are much too simplistic for predicting N_2O emissions. Alternately, if these trends extend to a larger database, i.e., if most lignites and subbituminous coals follow the prescribed trends, then the magnitude of N_2O emissions may be predicted with some certainty based on rank designations alone. In any case, a fundamental understanding of the chemistry of the Wyoming subbituminous coals may prove beneficial in reducing N_2O emissions.

Figure 2. The effect of temperature and coal rank on N_2O emissions.

Figure 3. The effect of excess air on N_2O emissions.

3.1.2 Effect of Excess Combustion Air

Figure 3 presents the effect of excess combustion air on N_2O emissions with four different coals. Increasing excess air in CFBC showed an increase in N_2O emissions when burning all coals. This apparent trend extends across all coal ranks tested and could be used to reduce N_2O emissions, to a limited extent, by using a minimal amount of excess air for combustion. There is also an interaction between excess air and temperature in relation to N_2O emissions--the effect of excess air level is stronger at lower temperatures than at higher temperatures. This can be seen in Figure 3 for the Salt Creek coal, which shows a much stronger dependence on excess air at 1074 K than for the data acquired at 1153 K. The data points for the other coals in this figure were obtained at approximately 1115 K. The disparity in slope between the various coals possibly indicates an interaction of coal rank with excess air, but is not conclusive from the limited data available.

3.1.3 Effect of Sorbent Feed

The effect of limestone feed on N_2O emissions is shown in Figure 4. Sorbent feed, in this figure, is expressed on a grams per MJ heat input basis. This places all coals on the same basis, unlike Ca/S ratio, which is only meaningful for comparing fuels having similar sulfur contents and heating values. The general trend for four of the five coals presented in this figure is a decrease in N_2O emissions with increasing sorbent feed. The opposing trend displayed for the Black Thunder subbituminous coal is not readily

Figure 4. The effect of limestone feed on N_2O emissions.

understood. This trend may be related to the composition of the coal or coal ash, since, from the data displayed in Figure 4, it is evident that interactions exist between sorbent feed and coal selection. The data for the bituminous coals suggest a potential N_2O emissions control strategy by increasing the sorbent feed rate. Unfortunately, the use of a limestone sorbent as a means of reducing N_2O emissions has been shown to result in a comparable increase in NO_x emissions. Therefore, the net result of this activity would be the conversion of N_2O to NO .

3.1.4 Effect of Primary/Total Air Ratio

The effect of combustion air staging into the primary and secondary zones was studied with Blacksville and Salt Creek bituminous coals. Figure 5 shows the effect on N_2O emissions of increasing the primary combustion air distribution in the combustor as a function of temperature and excess air level. As seen in this figure, the N_2O emissions appear to be affected by an interaction between primary air and temperature. At higher temperatures (1140 K), the N_2O emissions tend to decrease very slightly with increasing primary air split, while the opposite trend occurs at lower temperatures (1060 K). The effect of higher excess air for S3 data points (Salt Creek bituminous) indicates an interaction with primary air split, which contributes to the greater slope for this curve. These subtle effects, displayed in Figure 5, may be caused by changes in the dense-bed velocity and temperature profiles and are, therefore, indications of the interdependence of the operating parameters. Due to the limited data points defining the curves,

these results are considered preliminary until a better perception of the experimental error is established.

3.2 Impact of Coal and Operating Parameters

Figures 2 through 5 show that the operating parameters can have a significant effect on N_2O emissions and that the fuel specification controls the absolute magnitude of the emissions when the combustor is operated under similar conditions. In order to assess the relative contribution of individual operating parameters and fuel type on N_2O emissions, a comparison was made among these factors for firing Salt Creek bituminous coal. Since the operating parameters have been shown to interact with the fuel, this quantitative analysis cannot be extended to include other coals. Table 3 shows the effect of changing parameters relative to a reference nominal base condition of 40% excess air, 1116 K combustor temperature, 50% primary air split, and 63% sulfur retention by coal ash and sorbent (1.85-g sorbent/MJ). As seen in Table 3, sorbent feed will produce the greatest change in N_2O emissions, followed by temperature, excess air, and primary air, when based upon a unit change in the respective parameter. If switching to a Powder River subbituminous coal were a viable option, N_2O emissions could be reduced by 85% relative to firing Salt Creek coal under similar operating conditions.

In actual CFBC operation, the order of importance of the operating parameters in affecting N_2O emissions may vary due to practical design limitations and operating costs. For example, the reduction of excess air will result in lower N_2O emissions, but a practical lower limit exists for which combustion efficiency will be affected. Likewise, increasing excess air beyond 40% becomes prohibitively expensive for operation. For this reason, the impacts of the operating parameters and fuel type are best correlated by the net change in N_2O emissions for reasonable changes in operating conditions. The operating ranges depicted in the table are subjective and

TABLE 3

Effect of Operating Parameters on N_2O Emissions Firing Salt Creek Coal

Operating Parameters	Nominal Base	Change in Excess Air	Change in Sorbent Feed	Change in Primary Air	Change in Temperature	Change of Coal
Temperature, K	1116	1116	1116	1116	1172	1116
Excess Air, %	40	20	20	20	20	20
Primary Air Ratio, %	50	50	50	67	50	50
Limestone Feed, g/MJ	1.85	1.67	2.08	1.65	1.67	1.39
N_2O Emissions, mg/MJ	110	104	102	98	60	16
ΔN_2O , mg/MJ	0	-6	-2	-6	-44	-88
Δ Parameter	0	20%	0.41 g/MJ	17%	56 K	---
$\Delta N_2O/\Delta$ Parameter	---	-0.30	-4.88	-0.24	-0.75	---

Figure 5. The effect of primary air to total air ratio on N₂O emissions.

must be interpreted from this perspective. Based on the values presented in Table 3, the relative order of importance is given by fuel type > temperature > excess air, primary air split > sorbent feed rate for Salt Creek coal.

3.3 Parameterization of Coal Rank

The previous sections showed the significance of operating parameters and coal rank on N₂O emissions, with the major influence resulting from the particular coal type used in a combustor. In order to predict N₂O emissions through modeling, the effect of coal type needs to be parameterized into a set of readily measurable coal properties. This, in effect, will remove the "coal type" as a discrete variable and replace it with a continuous measure of an interaction with temperature and N₂O emissions. The relation of several parameters including coal nitrogen (N), oxygen (O), volatile matter (VM), fixed carbon (FC), and their ratios were used to correlate with the temperature dependence of N₂O emissions shown in Figure 2. The slopes of the linear best-fit lines in Figure 2 were used instead of absolute N₂O values since the lines do not converge to the same intercept. The absolute values would yield an infinite number of solutions (any vertical line through Figure 2). Additionally, all utility combustors require some degree of temperature excursion from the design specifications to account for load shifts. In this respect, an operating range of temperature/coal-type interactions is required to accurately predict N₂O emissions.

Figures 6 through 11 show the correlations of the coal property parameters with the rate of change of N₂O emissions (dependence) with

temperature. The popular approaches indicated in literature include VM, fuel ratio (FC/VM), and O/N ratio. These results are shown in Figures 6 through 8, respectively. The coal properties determined by proximate and ultimate analyses were normalized for heating value (kg of material/MJ of heat input). In effect, this quantity not only normalizes each coal for its heating value, but is also indicative of the actual flux of raw materials entering the combustor. As seen from these figures, only the O/N ratio provides a fair correlation when using a very diverse set of coals. The oxygen level in this ratio does not include oxygen from moisture. Figure 9 shows the temperature dependence of N_2O formation with the N/VM ratio. This figure shows a correlation very similar to that obtained for the O/N ratio, demonstrating a distinct separation of the lower- and higher-rank coals.

The coals used in this study, when placed on a moist, mineral-matter-free (mmf) heating value basis, should correlate to the approximate rank of the coal. This is only true for the coal rank series of lignite through high-volatile A bituminous due to the rank designations including both fixed carbon and heating value. If the trends are truly rank-dependent, then these rankings should correlate, in a broad sense, with the observed N_2O formation. Figure 10 shows the N_2O /temperature slopes as a function of corrected heating value. The figure shows that the dependence of N_2O emissions on coal rank is more closely preserved with the higher-ranked coals and that additional factors are required to discriminate between subbituminous and lignite coals.

Figure 6. The change in N_2O emissions with temperature versus the volatile-matter-feed rate.

Figure 7. The change in N_2O emissions with temperature versus the fixed-carbon to volatile-matter ratio.

Figure 8. The change in N_2O emissions with temperature versus the dry-basis oxygen to nitrogen ratio.

Figure 9. The change in N_2O emissions with temperature versus the nitrogen to volatile-matter ratio.

Figure 10. The change in N_2O emissions with temperature versus the moist, mineral-matter-free heating value.

Figure 11. The change in N_2O emissions with temperature versus the distribution of nitrogen in the fixed carbon and volatile matter.

As noted above, there are other important factors that are excluded from the analysis that would further improve the correlation between N_2O emissions and coal rank. These may include char surface characteristics, ash composition, sulfur concentration, and volatile matter composition. An attempt at improving the correlation is shown in Figure 11. The nitrogen in the coal and the coal char were determined, as aforementioned, in order to calculate the partitioning of nitrogen between the volatiles and the produced char. The simple relation of the sum of the ratios of nitrogen leaving in the volatile matter (N_v) to that of the nitrogen remaining in the char (N_c) was used as a possible explanation of the difference between N_2O emissions observed in the coal ranks. As presented in Figure 11, the N_2O formation correlated as well using this relation as with O/N, N/VM, and moist mmf heating value. Again, the higher-ranked coals tend to correlate better to this relation than the lower-ranked coals.

3.4 Preliminary Modeling

Statistical analysis of the experimental data was performed to i) screen the operational parameters for significance, and ii) quantify these parameters for use in an empirically derived model. An 80% confidence level was chosen for this analysis, with two, three, and four variables inputted simultaneously. The results of the modeling showed that, for any given coal, the relationships depicted graphically in Figures 2 through 5 could be adequately predicted. The major obstacle leading to a generalized model for predicting N_2O emissions from a CFBC is the effective parameterization of the coal. In addition, the effect of fuel parameters and their interactions with

operational parameters on N_2O emissions are still under investigation and have not been quantified for inclusion into a global model.

The partitioning of the coal nitrogen into the char and volatile matter and the O/N and N/VM ratios were shown as preliminary examples of parameterizing the effect of the fuel with temperature dependence. Using, as an example, the partitioning of fuel nitrogen as a means of describing the coal effects, the predictive equation for N_2O emissions, as derived through linear multiple regression analysis, takes the simplest form:

$$N_2O = A(\text{coal}) + B(\text{temp}) + C(\text{air}) + D(\text{sorbent}) + E(\text{primary})$$

where

N_2O = mg N_2O /MJ
 coal = effect of coal type
 temp = effect of temperature, K
 air = effect of excess combustion air, %
 sorbent = effect of limestone feed rate, g/MJ heat input
 primary = effect of primary to total air ratio, %

and

$A = a' + b'(\text{fuel variable})$
 $B = c' + d'(N_c/VM) + e'(N_c/FC)$ mg/MJ-K
 $C = f' - g'(\text{temp, K})$ ppm/% excess air
 $D = h'$ ppm/(g-limestone/MJ)
 $E = i'$ ppm/%primary air

where a' and b' are constants under development to determine the magnitude of the N_2O emissions with coal selection; c' , d' , and e' determine the dependence of N_2O emissions with coal and temperature; and f' through i' are determined by regression analysis of the database used for modeling coal and operational parameters. The constants a' and b' will be used to orient the curves presented in Figure 2, so that absolute N_2O values can be obtained from the slopes. It should be noted that this model and the statistically derived parameter coefficients are representative of the coals used in this experimental database. A generalized form of this empirical relation will require a broad base of fuels, with the accuracy dependent on the success of parameterizing the fuels in the database. Additionally, factors related to the scale and the mode of operation (bubbling versus circulating) of an FBC may be required to further enhance the accuracy of predicting N_2O emissions.

4.0 PUBLICATIONS AND PRESENTATIONS

During the course of the last reporting period, a major effort was made to interpret and disseminate the data that have been acquired to date. The bulk of the data thus far reported has been concerned with the effects of pilot-scale operating parameters and the selection of coals on N_2O emissions. In the future, the implications of coal-property effects will also be addressed due to the significant role the fuel has on establishing the magnitude of N_2O emissions.

The following is a list of publications and presentations that were commenced or finalized during this last reporting period:

1. "Nitrous Oxide Emissions in Fluidized-Bed Combustion: Fundamental Chemistry and Combustion Testing," a review to be published in *Progress in Energy and Combustion Sciences*.
2. "Nitrous Oxide Emissions in the Fluidized-Bed Combustion of Coal," presented at the 1992 Spring Meeting of the Western States Section of the Combustion Institute, March 23-24, 1992.
3. "Predicting N_2O Emissions from Circulating Fluidized-Bed Coal Combustion," to be presented at the 1992 Pittsburgh Coal Conference, October 1992.
4. "Pilot-Scale Studies on N_2O Emissions, Coal Properties, and Conditions in a Circulating Fluidized-Bed Combustor," 5th International Workshop on Nitrous Oxide Emissions, Tsukuba, Japan, July 1-3, 1992.
5. "Effect of Coal Rank and Circulating Fluidized-Bed Operating Parameters on Nitrous Oxide Emissions," submitted to *FUEL*.
6. "Nitrous Oxide Emissions from Fluidized-Bed Combustion," Workshop on Nitrous Oxide Emissions, presented at Morgantown Energy Technology Center, April 2, 1992.

This is a list of previous publications and presentations:

7. "Effect of Operating Parameters on N_2O Emissions in a 1-MW CFBC," Eighth Annual International Pittsburgh Coal Conference, October 14-18, 1991.
8. " N_2O Measurement in Coal-Fired Flue Gas," presented at the Seventh Annual Coal, Preparation, Utilization, and Environmental Control Contractors' Conference, Pittsburgh, PA, July 15-18, 1991.
9. "Mini-Workshop on N_2O Emissions from FBCs," presented at Morgantown Energy Technology Center, May 20, 1991.

5.0 REFERENCES

1. Anthony, E.J., Ed. *Proceedings of the 1991 Fluidized-Bed Combustion Conference, Nitrous Oxide Forums 1 and 2*; Montreal, Canada, April 1991, pp 677-730 and 985-1033.
2. Ramanathan, V.; Cicerone, R.J.; Singh, S.B.; Kiehl, J.T. *J. Geophys. Res.*, 1985, 90 (D3), 5547.
3. Henderson, A.K.; Moe, T.A.; Hajicek, D.R.; Mann, M.D. *In Proceedings of the Sixteenth Biennial Low-Rank Fuels Symposium*; May 1991, pp 407-420.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORTFORM APPROVED
OMB NO. 1800-0127
Page 1 of 2

1. Program/Project Identification No. DE-FC21-88MC10637	2. Program/Project Title Nitrous Oxide Emissions (4.6)	3. Reporting Period 3-1-82 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-6000		5. Program/Project Start Date 4-1-88
		6. Completion Date 9-30-92

7. FY 91/92	8. Months or Quarters Quarters	1991 JUL AUG SEP OCT NOV DEC	1992 JAN FEB MAR APR MAY JUN
9. Cost Status	a. Dollars Expressed in Thousands	b. Dollar Scale	
10. Cost Chart			
Fund Source	Quarter 1st 2nd 3rd 4th	Cum. to Date	Tot. Plan
DOE	P 75 75 75 74	299	299
	A 46 131 82 56	295	
	P		
	A		
	P		
	A		
	P		
	A		
Total P	75 75 75 74	299	299
Total A	46 131 82 56	295	
Variance	29 (56) 13 18	4	
P = Planned A = Actual		c. Cumulative Accrued Costs	
Total Planned Costs for Program/Project \$299		Planned	Actual
		75	46
		150	177
		225	239
		299	295
		Variance	
		29	(27)
		(14)	4

11. Major Milestone Status	Units Planned	Units Complete
A. Literature Survey	P	C
		No activities in current project year
B. Detailed Test Plan	P	C
		No activities in current project year
C. CFBC Testing	P	C
	1 2 3	
D. PFBC Testing	P	C
	1 2	
E. Bubbling-Bed Testing	P	C
	1 2 3 4	
F. Preliminary Engineering Model	P	C
	1 2	
G. Second Test Matrix	P	C
	1	

12. Remarks

Due to EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date

Michael E. Collins

14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Nitrous Oxide Emissions (4.6)		3. Reporting Period 3-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Literature Survey No activities in current project year				
Task B	Detailed Test Plan No activities in current project year				
Task C	CFBC Testing				
c.1	Lignite test	8-15-91	8-15-91		
c.2	Bituminous test	10-30-91	10-18-91		
c.3	Subbituminous test	11-30-91	11-22-91		
Task D	PFBC Testing				
d.1	ANL PFBC testing	7-15-91	7-15-91		
d.2	Report on PFBC test	11-30-91	12-31-91		
Task E	Bubbling-Bed Testing				
e.1	Coal type tests	11-30-91			
e.2	Sorbent tests	2-15-92			
e.3	Dry coal and char tests	4-30-92			
e.4	Mineral additive tests	6-30-92			
Task F	Preliminary Engineering Model				
f.1	Prepare preliminary model	12-31-91	12-31-91		
f.2	Update model	6-30-92	6-30-92		
Task G	Second Test Matrix				
g.1	Establish second matrix	11-30-91	12-31-91		

4.7 Pressurized Fluidized-Bed Combustion

PRESSURIZED FLUIDIZED-BED COMBUSTION

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

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July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

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PRESSURIZED FLUIDIZED-BED COMBUSTION

1.0 BACKGROUND

Pressurized fluidized-bed combustion (PFBC) has several advantages that make it attractive as a technology of the future, including:

- Increased efficiency and reduced capital and generating costs compared to pulverized coal-fired (pc-fired) boilers equipped with flue gas desulfurization (FGD).
- Modular units without the usual economy-of-scale penalty.
- Reduced combustor size, permitting shop fabrication and field erection, thereby greatly shortening construction lead time.
- High-sulfur fuels burned in the presence of sorbent in the fluidized-bed combustor (FBC) eliminating the need for FGD.
- Reduced combustion temperature (1400°-1700°F versus 3000°F for a pc-fired boiler), which results in significant reduction of NO_x emissions.
- Increased heat-transfer rate to the working fluid.
- Increased fuel versatility.
- Easily handled by-product material consisting of clinker-free, granular, smooth-flowing ash which may be easily disposed of for landfill uses or potentially sold for industrial or agricultural applications.

Major technical uncertainties identified by the industry as critical areas for PFBC commercialization are:

- Hot-gas cleanup for gas turbine protection, with particular reference to coal alkalis.
- Materials survivability for heat exchanger, gas turbine, and solids-handling equipment.
- Solids-handling improvement in feeding, distribution, and bed removal.
- Combustor configuration, including the heat-transfer bundles, distributor plate, fuels utilization, and operational parameters.

Some of these problems are being addressed by programs such as those at Grimethorpe and New York University. Others may be resolved during operation of three demonstration plants using first-generation technology: the AEP 70-MW_e Tidd Station at Brilliant, Ohio; the 79-MW_e Escatron Power Plant in Spain; and the 135-MW_e Energi Vartan Plant in Stockholm, Sweden. Although these plants show improved efficiency over atmospheric systems, they are still significantly below gas turbine efficiency. In an attempt to increase these

efficiencies, several companies are actively involved in the development of second-generation PFBC systems. The goals of the second-generation system are a 45% coal-to-electricity efficiency, a 20% cost-of-electricity advantage over pe-fired systems, modular design for shop fabrication, the capability to meet or exceed New Source Performance Standards (NSPS), and the ability to operate on a wide range of coals.

2.0 GOALS AND OBJECTIVES

The overall goal of the PFBC program at the Energy and Environmental Research Center (EERC) is to generate both fundamental and process information that will foster the development of an economical and environmentally acceptable second-generation PFBC concept. The goal is to focus on generic issues, such as the fate of alkali in PFBC systems, sorbent utilization, and carbonizer performance, while providing input to assist in the development of second-generation systems.

During the two years of this Cooperative Agreement (7/90-6/92), work focused on three main areas: carbonizer performance, fate of alkali, and increased sorbent utilization. Objectives are discussed below.

2.1 Carbonizer Performance Evaluation

In order for a second-generation PFBC to achieve 45% efficiency, it is likely that the coal must be partially gasified and the char residue burned in the PFBC. This will produce gas streams that can be cleaned at an intermediate temperature (e.g., 1600°F) and then afterburned to obtain temperatures higher than those obtainable directly from the PFBC, thereby increasing the efficiency of the gas turbine. Information needs to be generated to determine the extent of gasification desired to obtain the highest efficiency, while maintaining the benefits of the PFBC in terms of meeting environmental standards. The partial gasification step can be referred to by any of several terms, including carbonization, pyrolysis, or mild gasification.

The goal of this task is to use the existing EERC mild gasification reactor, with some modification, to develop a database at temperatures and pressures representative of those for a second-generation system, including:

- Determining gas, tar, and liquid yields for selected coals.
- Investigating the fate of sulfur and alkali.
- Studying the amount of tar generated, its properties, and its elimination, to determine its effect in the hot-gas cleanup device.

2.2 Fate of Alkali in PFBC Systems

Alkali in the coal, especially organically bound alkali, will volatilize even at the low temperatures typical of a fluid-bed gasifier or combustor. This alkali can cause problems in both the filter media and the turbine. The focus of this task is on developing an understanding of how the alkalies are released so that methods of rendering them harmless can be found. Alkalies gettering to keep the alkali in the bed is one potential method of protecting

the filter and turbine. Some work will be done on the pilot-scale bubbling and circulating atmospheric fluid beds. Because the vapor pressures of the alkali species are low and not greatly influenced by pressure, it is felt that data from the atmospheric units will be applicable to pressurized systems. Work will also be done on the bench-scale pressurized reactor. PHOEBE, a thermo-dynamic code for predicting gas-solid-liquid equilibrium stages, will be used as a tool to help predict trends with changing operating conditions and coal types.

2.3 Bench-Scale Reactor Testing

A bench-scale reactor to study PFBC reaction kinetics and conversions was designed around an already-existing piece of equipment to minimize costs. Design efforts attempted to minimize the impacts of the small size on the usefulness of the data, while providing for a wide range of conditions applicable to combustion and gasification in bubbling and entrained/circulating fluidized beds. A 3-inch ID reactor is envisioned. This reactor will be used to study sorbent utilization and alkali gettering. It is important to improve sorbent utilization to minimize the amount of sorbent feed and waste disposal. Extending the operating conditions where conventional sorbents are effective may help improve the overall efficiency of the PFBC. If properly designed, it is envisioned that this reactor could also be used for studying N₂O emissions, if time and budget allow.

2.4 Objectives of Current Year (7/91-6/92) Research

2.4.1 Task 1. Carbonizer Performance Evaluation

Baseline testing will be attempted using a Pittsburgh #8 coal and Plum Run dolomite. If successful operation can be maintained on the Pittsburgh #8, an experimental test matrix will be designed in collaboration with Foster Wheeler Development Corporation (FWDC) and the Morgantown Energy Technology Center (METC) so that a common database can be generated between the EERC system and that being built by Foster Wheeler. The establishment of a common point to allow scalability of data will allow other test data generated on the system to be used by Foster Wheeler when evaluating the impact of coal properties on the performance of the second-generation system.

If the baseline testing is successful, and if funds are available, parametric tests will be performed with other coals. Variables for these tests may include temperature, pressure, velocity, coal and sorbent type and size, and sorbent calcium-to-sulfur ratio. The goal is to collect process data on the formation of agglomerates and clinkers; tar-vapor condensation; the stickiness of the char-sorbent-elutriated effluent; levels and forms of sulfur and nitrogen; levels, forms, and phases of alkalies; yields, composition, and heating value of effluent; effects of tar cracking on sorbent-sulfur-capture effectiveness; and char physical characteristics. The coal and sorbent types tested and the test matrix will be reviewed with FWDC and METC before testing.

2.4.2 Task 2. Fate of Alkali in PFBC Systems

Several good thermochemical models are available to help predict the equilibrium concentrations of the solid, liquid, and gaseous species as a function of temperature and pressure. Two of these models, PHEOBE and SolGas

Mix, are used as tools to predict how changes in coal types and operating conditions will affect the amount and type of alkali released. This information is used in conjunction with results of bench- and pilot-scale work.

Some bench-scale work will be done using thermogravimetric analysis (TGA) and the pressurized drop-tube furnace. The purpose of this work is to look at the impact of coal type on the release of alkalies. The form of the alkali in the raw coal can significantly affect the quality of alkali released in the vapor and that retained within the original minerals of the coal.

Since techniques such as thermogravimetric analysis and drop-tube furnace tests cannot simulate the turbulent mixing of burning coal, and sorbent particles cannot provide the fluid dynamics of an FBC, alkali studies will also be performed on the bench-scale PFBC and on the pilot-scale atmospheric bubbling and circulating FBCs. The main purpose of this testing is to investigate the use of ash matrix modifiers to capture alkali in the bed. Conditions such as pressure, temperature, oxygen level, and ash modifier type will be investigated. An end goal of this phase is to find a material that can reduce both alkali and sulfur levels.

2.4.3 Task 3. Bench-Scale Reactor Testing

The bench-scale reactor designed during the previous program year will be constructed. The design calls for a 3-inch ID reactor vessel capable of operating up to 150 psi and 1800°F. Provisions will be made to sample at several locations in the bed and freeboard, with the hope of freezing reactions so that reaction pathways and kinetics can be determined. The design goals of this reactor are to study alkali release, ash modification, and sorbent utilization. Nitrous oxide emissions could also be studied.

As a part of this task, the bench-scale testing will focus on sorbent utilization for PFBC applications. A fundamental understanding and prediction of sulfur-capture efficiency for alkaline ash and limestone/dolomite sorbents over a wide range of conditions will be developed. Performance in both the carbonizer and combustor are important. During carbonizer testing, a sulfur balance will be performed to determine the form and product stream in which the sulfur will be present. Bench-scale tests will attempt to improve the overall sulfur capture. Potential advancements to the industry include improving the utilization of the sorbent material and extending the range of operating conditions in which sorbents are effective.

3.0 RESULTS AND DISCUSSION

3.1 Carbonizer Performance Evaluation

3.1.1 PFBC PDU Operation Summary During P022

The modified 100-lb/hr mild gasification process development unit (PDU) was run as a PFBC carbonizer to evaluate the use of Pittsburgh No. 8 bituminous coal under second-generation PFBC operating conditions. The experimental matrix for this test was discussed in the July through December 1991 semiannual technical report for this project. The test, P022, was

conducted on December 2-3, 1991, and consisted of three run periods. Run conditions are presented in Table 1, and a description of the run is contained in the following paragraphs.

The carbonizer was pressure-tested and then heated at atmospheric pressure to the reaction temperature (1600°F) using methane. (Additional heat was supposed to have been supplied using propane, but condensation in the feed line from the propane tank to the system prompted the change to methane.)

TABLE 1
Carbonizer Test P022 Run Conditions

	Run Period		
	1	2	3
Coal	Wyodak	Wyodak	Pittsburgh No. 8
Wt. Dolomite/Wt. Coal	0.3	0.3	0.3
Dolomite/Coal Feed Rate, lb/hr	94	94	54.1 ^a
Temperature, °F	1625	1625	1625
Pressure, psig	7	56	56
Gas Flow Rates, scfh			
Air	2187	3934	2919
Tempering N ₂	0	2506	340
Transport N ₂	387	1817	440
Purge	7	111	500
O ₂	310	294	204
CH ₄	177	312	255
Total	3068	8974	4658
Superficial Velocity ^b	6.1	5.6	2.8
Air/Coal, scfh/lb per hr	30.2	54.4	70.2

^a Average value, feed rate increased during the run period.

^b At reaction conditions.

Agglomeration had been noted during earlier tests using Pittsburgh No. 8 bituminous coal. Therefore, to ensure a successful system start-up, the run was initiated using Wyodak subbituminous coal, and the first run period consisted of operation using Wyodak coal at 7 psig (1.5 atm) and 1625°F. Char, condensate, and product gas samples were quantitatively taken during this run period.

Once steady-state conditions were achieved during the first run period, the pressure was increased and the unit allowed to come to steady state again. The second run period consisted of operation of the unit on Wyodak coal at 1625°F and 56 psig (4.8 atm). Product gas samples were taken during this run period, but condensate and char samples were not.

The changeover to Pittsburgh No. 8 coal was scheduled to take place gradually to minimize the possibility of agglomeration. The system was to be fed a mixture of Wyodak and Pittsburgh No. 8 coals and allowed to reach steady-state conditions. At that point, Pittsburgh No. 8 coal was to be introduced at a slow feed rate, increasing in 20-lb/hr increments and allowing the system to reach steady state.

The changeover to Pittsburgh No. 8 coal was not as gradual as had been planned. When the pressure was maintained at 56 psig (4.8 atm) and the temperature at 1625°F, the feed was abruptly changed from Wyodak to Pittsburgh No. 8 coal. The coal/dolomite feed rate was increased over the course of the entire third run period, from 20 lb/hr to 80 lb/hr. A hot spot developed on the side of the vessel where an unused nozzle had been insufficiently insulated, and the run was terminated. Following shutdown, no evidence existed of the extensive agglomeration of the Pittsburgh No. 8 coal that had occurred during the earlier attempts to carbonize it. A product gas sample was taken during the run period, and the char present in the cyclones and the char hopper at the end of the run was collected. A sample of the condensate was not taken during this run period.

3.1.2 Analytical Protocol of Samples Taken During P022

The product gas samples that were collected during P022 were analyzed by gas chromatography. Char samples were analyzed for moisture, fixed carbon, volatile matter, and ash contents (proximate analysis); for C, H, N, S, and O (by difference) contents (ultimate analysis); and via x-ray fluorescence analysis to determine the inorganic constituents of the ash. The condensate was filtered and the solids subjected to determination of moisture, volatile matter, fixed carbon, ash, and sulfur contents; heating value; and solubility in tetrahydrofuran (THF). The condensate liquids were analyzed for total organic carbon and total phenolic contents. The density of the liquid fraction of the condensate was also determined.

3.1.3 Data Reduction and Model Modification

A good mass balance could only be performed for the first run period due to the lack of quantitative samples. Mass and material balances were performed for this run period and yielded the data presented in Table 2. An elemental balance over this run period is shown in Table 3. The elemental balance presents the values for H and O on a dry basis; therefore, a water balance is also included.

Because the data necessary to perform the mass balances were unavailable, the yield structure for the third run period (performed with Pittsburgh No. 8 coal) was determined in an alternate manner. The computer model of the mild gasification unit, that had been developed for use in determining the various gas flows necessary to meet the experimental matrix conditions, was modified to predict the product slate of carbonization. The model was originally developed using three steps:

1. Input of the flow rates and analyses of the feedstocks.
2. Description of the chemical reactions occurring within the vessel with respect to the production of heat (i.e., burning methane and/or coal).

TABLE 2
Material Balance for P022 Run Period 1
with Wyodak Coal^a

<u>In</u>	
Coal Feed	
Wyodak (maf ^b basis)	450
Dolomite + Ash	200
Water	118
Gas Feed	
Air	1436
N ₂	251
CH ₄	53
O ₂	226
Scrubber Water	269
<u>Out</u>	
Solids	
Char (maf basis)	62
Ash	91
Water	5
Condensate	294
Product Gas	
O ₂	21
H ₂	30
CO ₂	577
N ₂	1430
CO	402
CH ₄	22
H ₂ O	5.6
Char Yield	11.2%
Closure	98.14%

^a All weights in lb.

^b Moisture- and ash-free.

3. Performance of a heat balance over the system to obtain an estimate of the reactor heat loss.

Additional information was added to the model so that it could be used to predict the yield structure of the carbonizer tests. The following information was incorporated during modification of the model:

4. Description of the chemical reactions taking place within the carbonizer.

TABLE 3
Elemental Balance for P022 Run Period 1
with Wyodak Coal^a

	In	Out
C	408	399
H ^b	38	38
N	1357	1431
S	1	1
O ^b	713	688
Ash	99	93
Water	387	299

^a All weights in lb.

^b Moisture-free basis.

Several reactions take place within the vessel proper, including the combustion of methane ($\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$); the reaction of the methane combustion-produced water with carbon in the coal ($\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2$); the combustion of carbon in the coal ($\frac{1}{2}\text{O}_2 + \text{C} \rightarrow \text{CO}$; $\text{O}_2 + \text{C} \rightarrow \text{CO}_2$); the reaction of coal moisture with carbon in the coal ($\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2$); pyrolysis of the coal, resulting in approximately equal molar ratios of H_2O and CO_2 (in which the reaction is essentially $\text{CH}_2\text{O}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2$); the reaction of the pyrolysis water with carbon in the coal ($\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2$); and, finally, the production of CO_2 during heating of the dolomite.

5. Development of chemical boundary machine constants based upon the behavior of the system during operation using Wyodak coal.

Approximately 41.5 mol% of the methane and 23.5 mol% of the oxygen channeled during the first run period with Wyodak coal. About 20 mol% of the water available for reaction did not react and left the system with the product gas. Three assumptions were made with respect to the chemical reactions taking place in the reaction vessel: 1) the ratio of CO to CO_2 produced during carbon combustion was 0.35 to 0.65, 2) approximately 35 mol% of the elemental hydrogen present in the dry coal went to the production of pyrolysis water, and 3) the dolomite weight loss was assigned entirely to the production of CO_2 .

6. Determination of the quantity of char produced.
7. Determination of the quantity and speciation of product gases.
8. Performance of mass and material balances on the system and the inclusion of this information in the model.

9. Performance of an elemental balance over the vessel proper.
10. Definition of the fourth reaction zone (in the water scrubber) and the reactions occurring there.

The hot product gas, rich in CO, was contacted with water in the scrubbers. The gas temperature at this point was high enough for the water/gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) to take place.

11. Verification of mass, material, elemental, and heat balances for the entire system.

Figure 1 is a diagram of the reaction zones that occur in the system.

3.1.4 Discussion of Results

Once completed, the model was used to predict the product slate of the first run period. This predicted product slate is compared to the actual product slate in Table 4. As the table shows, the model accurately predicts the product slate for the run period using Wyodak subbituminous coal. There is little reason to expect that it could not also be successfully used to predict the product slate of the carbonization of Pittsburgh No. 8 bituminous coal.

Figure 1. Reaction zones included in the predictive model.

Due to differences between the Wyodak and Pittsburgh No. 8 coals, it was assumed that slightly less elemental hydrogen would go to the production of pyrolysis water (33% rather than 35%). It was also assumed that the amount of water that did not react increased from 19.9 mol% to 30 mol% and that the ratio of CO to CO₂ produced during combustion of the carbon decreased from 0.35:0.65 to 0.10:0.90.

Table 5 compares the predicted product slate for run period 3 with the actual product slate (such as could be calculated) from the Pittsburgh No. 8

TABLE 4
Comparison of Predicted P022 Run Period 1 Product
Slate with Actual Product Slate^a

Coal:	Predicted Wyodak	Actual Wyodak
Product Gas, lb		
O ₂	66	21
H ₂	30	30
CO ₂	617	577
N ₂	1355	1430
CO	410	402
CH ₄	27	22
H ₂ O	5.5	5.6
Total	2510.5	2487.6
Condensate, lb	322	294
Char (maf ^b), lb	62	62
Dolomite + Ash, lb	110	91
Water in Char, lb	4.9	4.7
Closure	100%	98.14%
Char Yield	13.8%	11.2%

^a Total quantities produced during run period with Wyodak coal.

^b Moisture- and ash-free.

run period. Not all values could be compared due to the lack of samples, but the predicted and actual gas product slates agree fairly well. The char samples collected during this run period were taken from the char hopper and the cyclones. The ultimate analysis of the char in the char hopper was quite different from that of the cyclone fines, as can be seen in Table 6. Based upon the quantities collected from each location during the Wyodak run period, these values were weighted to arrive at an average char analysis, which is shown in Table 5. The predicted and average values agree fairly well when it is taken into account that small real differences at this scale can result in

TABLE 5
Comparison of Predicted P022 Run Period 3 Product
Slate with Actual Product Slate^a

Coal:	Predicted Pittsburgh #8	Actual Pittsburgh #8	
Product Gas, lb			
O ₂	21	5	
H ₂	6	3	
CO ₂	175	119	
N ₂	686	750	
CO	45	37	
CH ₄	12	8	
H ₂ O	6.6	-- ^b	
Total	951.6	--	
Condensate, lb	26.4	--	
Char (maf ^c), lb	22.5	--	
Dolomite + Ash, lb	25.5	--	
Water in Char, lb	0.2	--	
Char Analysis, wt% maf coal			
H	3.14	0.67	Weighted average of all analyses ^e
C	72.31	72.04	
N	2.17	0.98	
S	10.48	3.34	
O ^d	11.91	22.96	
Closure	99%	--	
Char Yield	25.6%	--	

^a Total quantities produced during run period with Pittsburgh No. 8 coal.

^b Information not available.

^c Moisture- and ash-free.

^d By difference.

^e Ranges of analyses are given in Table 6.

dramatically different percentages. It should also be noted that most of the predicted values fall within the range defined by the two char analyses.

Based upon the product slate predicted using the computer model, it appears that operation at 1625°F, 4.8 atm, and the gas flow rates noted in Table 1, results in a char yield of approximately 25 wt% of the Pittsburgh No. 8 coal fed to the system.

3.2 Bench-Scale Reactor Testing

A pressurized fluidized-bed (PFB) reactor has been designed and is being constructed to allow extensive alkali and hot-gas cleanup testing on a cost-effective manner over a wide range of operational conditions. A side view of

TABLE 6
Elemental Analysis of Char and Cyclone Fines
From P022 Run Period 3^a

	Char Hopper	Cyclone Fines
H	0.91	0.54
C	90.10	62.99
N	1.37	0.76
S	9.29	0.05
O ^b	-1.69	35.64

^a All values in wt% on a moisture- and ash-free basis.

^b By difference.

the reactor and cyclone are shown in Figure 2. Preheated fluidizing gas at temperatures up to 1000°F and pressures up to 150 psig will be supplied at the bottom of the reactor through a 1-in schedule 40 pipe at sufficiently high velocities to prevent the sized bed material from dropping out during operation. Bed material can be sampled or collected using a lock hopper system located at the bottom of the reactor. The fluidizing gas enters into the 3-in schedule 80 main section of the reactor through a conical transition. The operating velocities in the 3-in section will allow some internal recirculation of the fluidized-bed material. External heaters will be used for heating and maintaining the reactor and hot cyclone at temperatures up to 2000°F for atmospheric operation and up to 1700°F for operation at 150 psig.

Limestone, inert bed material, or ash generated from a combustor or by an ashing procedure can be added at the start of a test using a lock hopper system. Selected additives and coal can be fed separately at controlled rates during testing. Coal feed, when utilized, will be maintained at a low rate to eliminate any heat removal requirements from the reactor. Fluidizing gas can be supplied as air or as various mixtures of nitrogen, oxygen, carbon dioxide, carbon monoxide, sulfur dioxide, and nitrogen oxides to result in a flue gas similar to that generated in a full-scale fluidized-bed boiler. Different oxidizing and reducing condition tests can also be conducted. An alkali sampling probe can be inserted through the top of the reactor or through the top of the hot cyclone for when hot-gas cleanup testing is being conducted.

Figure 2. Side view of pressurized fluidized-bed reactor.

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORTFORM APPROVED
OMB NO. 1900-0127
Page 1 of 2

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Pressurized Fluidized-Bed Combustion (4.7)	3. Reporting Period 3-1-92 through 8-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-86
		6. Completion Date 8-30-92

11. Major Milestone Status	Units Planned	Units Complete
1. Carbonizer Performance Evaluation	P	a ▽ b, c, d
	C	
	P	
	C	
2. Fate of Alkali in PFBC Systems	P	a ▽ b ▽ c ▽ d A
	C	
	P	
	C	
3. Bench-Scale Reactor Testing	P	a ▽ b A
	C	
	P	
	C	
4. Sulfation of FWDC Bed Material	P	a A
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks

Due to EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date

14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Pressurized Fluidized-Bed Combustion (4.7)		3. Reporting Period 3-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-86	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task 1	Carbonizer Performance Evaluation:				
1.a	Perform baseline tests	12-31-91	3-31-92		
1.b	Develop process data on other coals	6-30-92			
1.c	Identify operability constraints	6-30-92			
Task 2	Fate of Alkali in PFBC Systems:				
2.a	Recommendation of modifiers to FWDC	10-1-91			
2.b	Modeling studies	11-15-91	3-31-92		
2.c	Bench-scale studies	3-31-92	*		
2.d	Ash modification/pilot scale	6-30-92	*		
Task 3	Bench-Scale Reactor Testing				
3.a	Sulfur balance on carbonizer	12-31-91	5-31-92		
3.b	Bench-scale studies	6-30-92			
Task 4	Sulfation of FWDC Bed Material	6-30-92			
	* Tasks replaced by Task 4				

5.0 LIQUEFACTION RESEARCH

5.1 Low-Rank Coal Direct Liquefaction

LOW-RANK COAL DIRECT LIQUEFACTION

**Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992**

by

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LOW-RANK COAL DIRECT LIQUEFACTION

EXECUTIVE SUMMARY

The Energy and Environmental Research Center has developed a multistep direct liquefaction process designed specifically to take advantage of the positive characteristics of low-rank coals (LRCs). The steps consist of 1) a pretreatment soak at very low-severity conditions in a hydrogen-donating solvent, 2) a solubilization step in which most of the coal dissolves in a process-derived solvent under relatively low-severity conditions, 3) a polishing step in which hydrogen gas and a process-derived solvent are added to the system to solubilize the remaining coal, and 4) hydrotreatment using hydrogen gas and a catalyst.

The entire multistep sequence was preliminarily investigated during the period from January through June 1992. Four complete run sequences were performed, including 1) pretreatment of an Indian Head lignite/hydrogenated, coal-derived anthracene oil (HA061) slurry at 175°C and 2100 psi with Ar and H₂S; 2) solubilization at either 350° or 375°C and 3500 psi with CO; 3) polishing using cresylic acid at either 435° or 460°C and 3200 psi with H₂; and 4) hydrotreatment in HA061 vehicle solvent at 425°C and 3500 psi with H₂ and Shell 424 catalyst. The hydrotreatment was performed until no significant hydrogen uptake was noted in order to define the upper range of hydrotreatability of the slurry. Testing was performed in the EERC's hot-charge, batch autoclave system. Products were analyzed for tetrahydrofuran (THF) solubility and ash and water content.

Mass and material balances were performed for the series, and the analytical results were incorporated. The resulting yield structures define the hydrotreated products of the entire four-step system based upon moisture- and ash-free (maf) coal fed to the pretreatment step. The most successful series (N562) resulted in a conversion of 96.64 wt% of the maf coal fed to the system. Of that total, 17.27 wt% consisted of gaseous products, 66.04 wt% consisted of premium distillate, 4.12 wt% consisted of soluble residuum, and 9.13 wt% consisted of light oxygenate material.

1.0 INTRODUCTION

To expand the scientific and engineering database of low-rank coal (LRC) liquefaction, investigations of direct liquefaction processes that produce the most competitive feedstocks or liquid fuels must be investigated. Coal can be converted to very high yields of oils with increasing levels of efficiency using a two-stage processing approach. Current two-stage direct liquefaction processes are usually performed with high-rank coals at temperatures greater than 400°C and pressures of approximately 2500 psi. Catalysts, which are very expensive, are generally used in both stages. While the economics of direct liquefaction have improved during the last five years, it is not yet a commercially viable method of producing liquid fuels due to its use of catalysts in both stages and the severity of the conditions employed.

Work performed early in the 1980s showed that LRCs are very reactive. It seems logical that they could be cost-effectively substituted into the direct liquefaction process since they would most likely require less severe reaction conditions. However, most attempts to use LRCs during direct liquefaction have not been successful because the coal reacts too rapidly for the available hydrogen source(s), resulting in the production of retrograded material. Any successful use of LRCs in direct liquefaction will require that advantage be taken of their positive characteristics.

This is the view taken by the EERC, which sees the initial solubilization of coal in the solvent as reverse coalification and the subsequent upgrading as reforming or refining. Under this scenario, it is assumed that the structure of coal is composed of physically and chemically tangled, highly cross-linked molecules. The molecular structures of premium distillate fuels (the desired product), by comparison, are discrete molecules of similar size and chemical nature, having virtually no chemical or physical attachments. The goal, therefore, is to go from a chemical knot to an orderly structure. The first phase in liquefaction should be to "untangle" the coal structure (at low-severity conditions to prevent coalification [retrograde] reactions), while the second phase should be to "organize" the untangled pieces so that those of similar size and chemical nature are first separated from the remaining material and then stabilized to prevent back reactions.

Through funding provided under the Cooperative Agreement, the EERC has been working on this concept for a number of years and has developed a process specifically designed for LRCs that consists of four steps, only the last of which is catalytic. The first step is a pretreatment soak at very low-severity conditions (175°C) in a hydrogen-donating solvent. (This is analogous to the coal-drying step currently performed prior to liquefaction processing. Drying is usually performed at approximately 115°C.) The purpose of this step is to place hydrogen or radical-capping agents in a location so that they are available to the coal when needed during the "untangling" portion of the reaction. The second step is a solubilization ("untangling") step, in which most of the coal dissolves in a process-derived solvent under relatively low-severity conditions. The third is a polishing step, in which hydrogen gas and a process-derived solvent are added to the system to solubilize the remaining coal. (Low-rank coals tend to produce phenolic material as they undergo liquefaction; the highest probability of dissolving them would be in a solvent similar to such a coal-derived solvent.) The final, or "organizing" step, consists of hydrotreating the solubilized coal using a catalyst and hydrogen gas under moderately severe conditions. It may

be possible to increase the conversion to upgraded liquids, and/or improve the product slate, and/or lower the reaction severity required during the fourth step (hydrotreatment) if appropriately solubilized material is produced during the first three steps (pretreatment, solubilization, and polishing).

2.0 GOALS AND OBJECTIVES

2.1 Three-Year Program Beginning FY'89-90

The primary objective of the three-year Low-Rank Coal Direct Liquefaction program has been to develop an LRC liquefaction process that will result in increased levels of conversion to distillable liquids. The work effort associated with meeting this objective has included an investigation of low-severity preconversion treatment of LRCs and a mechanistic study of the retrograde reactions which occur during processing as a function of conversion. Through mechanistic inference, the results of this work may be applicable to higher-rank coals.

The potential role of preconversion treatment of LRCs has been evaluated empirically by determining which systems can successfully prepare LRCs for thermal first-stage conversion during two-stage processing. The initial work screened various proposed systems for their effect on first-stage conversion. Second-year work focused on promising systems identified during the initial screening, evaluating them more fully with respect to their impact on thermal first-stage processing.

Preliminary evaluation of the use of hydrogen-donating solvents during preconversion treatment was performed on the batch scale. The products from the batch-scale pretreatment tests were subjected to two-step, thermal first-stage processing to determine the effects of pretreatment on the first-stage yield structure. The results were compared to those of previous tests performed with a nonhydrogen-donating solvent.

A preliminary mechanistic study of the retrograde reactions that occur as a function of typical liquefaction processing was scheduled for the first year. For this study, samples were produced at low-severity processing conditions with conversions of 10%, 50%, and 95%. An additional test was performed at more severe conditions to produce a coked product. Analysis of the products of the tests indicated which changes occur in the products with respect to increasing conversions to soluble material. A relatively detailed examination of the fate of the chemical functional groups present in the coal was provided by ^{13}C NMR analysis. This technique made it possible to observe and follow specific retrograde trends, expanding on the knowledge necessary to devise a more efficient processing scenario for LRCs.

2.2 Third-Year (FY'91-92) Work Plans

Specific work scheduled for FY'91-92 has undergone several changes in scope. The following paragraphs describe the tasks as they were, or will be, performed.

Task 1 consisted of the integration of pretreatment (Step 1) with low-severity first-stage processing developed during earlier EERC work (Step 2 plus Step 3), followed by hydrotreatment (Step 4) of the solubilized product.

The best of the pretreatment schemes studied was added to first-stage processing at conditions that, during the transition quarter of FY'88-89, provided the most favorable yield structure for LRCs. Hydrotreatment was performed at conditions that would result in the maximum possible upgrading.

Task 2 was eliminated when Task 1 was amended to include the hydrotreatment step.

Task 3 consists of the preparation of the final project report covering the period July 1, 1989, through the end of the project (including the proposed work mentioned in Section 3.2). The final report will summarize all of the information gathered during the integration of the EERC multistep, two-stage liquefaction process.

3.0 ACCOMPLISHMENTS

3.1 FY'91-92 Task 1--Further Investigation of Pretreatment and Lower-Severity Processing

As mentioned in Section 1.0, the EERC has developed a four-step liquefaction process consisting of:

- Step 1 - Pretreatment, which was investigated during FY'89-90 and FY'90-91.
- Step 2 - Solubilization.
- Step 3 - Polishing, which was investigated during FY'88-89, Task K.
- Step 4 - Hydrotreatment.

The first three steps comprise the thermal first stage of liquefaction, but have never been performed as part of an integrated run scheme. The objective of the FY'91-92 Task 1 test matrix was to add the polishing step (Step 3, a 20-minute, or less, reaction with H_2 at 425°C) to the best pretreatment-solubilization combination tested during FY'90-91 (i.e., pretreatment under Ar and H_2S at 175°C and 2000 psi for 60 minutes, followed by solubilization under CO at 375°C and 3500 psi for 60 minutes). Due to the promising results obtained during the FY'90-91 studies, it was decided that the annual project plan would be amended to include hydrotreatment of the products of the integrated three-step sequence.

3.1.1 Methods and Materials

The test matrix for Task 1 is presented in Figure 1. As the figure shows, the testing was performed according to a tree diagram-type of matrix. Performing the tests in this manner, i.e., using the same feed slurry whenever possible, enabled direct comparisons to be made between the run sequences. Two Step 1 runs were performed at identical conditions to obtain sufficient pretreated slurry for the remaining processing. The pretreated slurries from these two runs, N553 and N554, were combined into a bulk sample. (All analyses were performed on the bulk sample rather than on the individual pretreated slurries.) Pretreated slurry was then solubilized in two batches, one at ~375°C (N555) and one at ~350°C (N556). The solubilized products of

each of these Step 2 runs were polished (Step 3) at either 460°C (N558 or N557) or 435°C (N559 and N560) with a small amount of added cresylic acid. Each polished product was combined with a heavier vehicle solvent (hydrogenated anthracene oil) and distilled to remove a quantity of water and light, highly oxygenated solvent/coal-derived liquid equal to that added during the polishing step. Finally, each of the polished product slurries from Step 3 was hydrotreated in Step 4 (N562, N564, N563, and N566, respectively). The multistep run sequences are referred to in this report by the run numbers of their hydrotreatment steps. The specific run solvents, additives, and conditions for each step of the four run sequences are given in Table 1.

Figure 1. Run sequences tested during FY'91-'92 Task 1.

TABLE 1

Conditions of Task 1 Run Series

	N562	N563	N564	N565
<u>Step 1 - Pretreatment</u>				
Run No.	N553+N554	N553+N554	N553+N554	N553+N554
Solvent	HA061 ^a	HA061	HA061	HA061
Additive	H ₂ S	H ₂ S	H ₂ S	H ₂ S
Gas	Ar	Ar	Ar	Ar
Avg. Temp., °C	179	179	179	179
Max. Temp., °C	184	184	184	184
Avg. Pressure, psi	2064	2064	2064	2064
Max. Pressure, psi	2100	2100	2100	2100
Residence Time, min	60	60	60	60
<u>Step 2 - Solubilization</u>				
Run No.	N555	N556	N555	N556
Feed	N553+N554	N553+N554	N553+N554	N553+N554
Additive	None	None	None	None
Gas	CO	CO	CO	CO
Avg. Temp., °C	375	353	375	353
Max. Temp., °C	385	354	385	354
Avg. Pressure, psi	3488	3460	3488	3460
Max. Pressure, psi	3600	3515	3600	3515
Residence Time, min	60	60	60	60
<u>Step 3 - Polishing</u>				
Run No.	N558	N559	N557	N560
Feed	N555	N556	N555	N556
Additive	CA1 ^b	CA1	CA1	CA1
Gas	H ₂	H ₂	H ₂	H ₂
Avg. Temp., °C	435	433	458	461
Max. Temp., °C	437	435	461	465
Avg. Pressure, psi	3190	3363	3200	3439
Max. Pressure, psi	3226	3435	3275	3540
Residence Time, min	20	20	20	20
<u>Step 4 - Hydrotreatment</u>				
Run No.	N562	N563	N564	N566
Feed	N558	N559	N557	N560
Additive	Shell424	Shell424	Shell424	Shell424
Gas	H ₂	H ₂	H ₂	H ₂
Avg. Temp., °C	423	424	422	420
Max. Temp., °C	426	425	426	421
Avg. Pressure, psi	3459	3461	3525	3554
Max. Pressure, psi	3655	3635	3675	3675
Residence Time, min	180	180	180	180

^a Hydrogenated coal-derived anthracene oil.^b Cresylic acid solvent.

Testing was performed in the EERC hot-charge, batch autoclave system. The 1-gal autoclave was used when larger quantities were processed (i.e., during Steps 1 and 2 [pretreatment and solubilization]). The 1-L autoclave was used for the polishing and catalytic upgrading (Steps 3 and 4). Karl Fischer water, ash, and THF solubility analyses were performed on the feed and product slurries. Due to a lack of funding, elemental analyses were performed for only a few runs.

3.1.2 Discussion of Results

Mass and material balances were performed for the run sequences based upon maf coal fed to the pretreatment step. Allowances were made for the removal of sample aliquots for analysis. Combining the analytical results and the material balances resulted in the calculation of product slates for the integrated run series. In other words, product slates were calculated for the entire four-step system based upon maf coal fed to the pretreatment step. These product slates are presented in Table 2.

Tables 3 and 4 summarize this information and organize it in a simplified manner to permit easier comparisons between run series. As seen in Table 3, comparison of solubilization (Step 2) at 350° and 375°C shows that higher-temperature solubilization ultimately resulted in less gas + water production (about 17 wt% compared to 34 wt%) and more total liquid product (about 70-80 wt% compared to 59 wt%) than solubilization at the lower temperature. More of the hydrotreated liquid product was in the form of premium distillate (66 wt% compared to 31-56 wt%) when the slurry had been solubilized at 375°C.

When the polishing (Step 3) temperatures are compared, it can be seen that the higher-temperature polishing (~460°C) resulted in yields that were similar to those of the lower-temperature polishing (~435°C), but that the liquid product slates were very different. This is especially noticeable for N563 and N566, the run series with 353°C solubilization. The lower-temperature polishing step resulted in substantial differences in yields of distillate, soluble resid, and oxygenates. In this case, the higher polishing temperature seems to have cracked more of the coal-derived material, resulting in the production of far more oxygenates at the expense of distillate production. The higher polishing temperature also resulted in an increased production of soluble resid. The same differences were present, but not as obvious for the N562 and N564 run series with 375°C solubilization. Slightly more distillate and soluble resid were produced when the higher polishing temperature was used, but far fewer oxygenates were produced. The highest overall conversions were produced when polishing was performed at the lower temperature. The higher polishing temperature seems to have retrograded some of the coal-derived material (probably the phenolic material), resulting in a conversion loss at the expense of the production of the oxygenates.

A comparison of the gas + water yields is presented in Table 4. As the table shows, 2.0 wt% of the maf coal fed to the system was removed during the pretreatment (Step 1) as gaseous products. Twice as much of the maf coal left the system as gas during both the solubilization and polishing steps (Steps 2 and 3, respectively) when the solubilization was performed at ~350°C. The gaseous product slates of the polishing step were very different for the run series performed at higher solubilization temperatures compared to those performed at lower solubilization temperatures. It appears that more CO₂ is

TABLE 2

Product Slates of Task 1 Run Series^a

Hydrotreatment Run No.	N562	N563	N564	N566
Solubilization Temp., °C	375	353	375	353
Polishing Temp., °C	435	433	458	461
Gas Out				
CO	-65.92	-36.92	-63.20	-36.44
H ₂	-1.50	-0.93	-5.46	-2.64
CO ₂	114.26	93.05	116.00	93.65
C1-C3	11.53	13.50	11.70	14.38
H ₂ S	1.48	0.58	0.92	0.42
H ₂ O	-42.57	-34.12	-42.27	-35.32
Total Gas + Water	17.27	35.16	17.68	34.04
Liquid Out				
Oxygenated Liquids	9.13	-0.13	2.49	17.77
Premium Distillate	66.04	56.35	67.08	31.46
Soluble Residuum	4.12	3.33	3.26	9.00
Total Liquids	79.29	59.55	72.83	58.23
Unconverted IOM	3.36	7.60	9.12	6.43
Total, All Products	99.93	102.31	99.64	98.70

^a Product slates given include all steps (pretreatment, solubilization, polishing, and hydrotreatment) and are based upon percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

TABLE 3

Comparison of Effect of Solubilization and Polishing Temperatures on Final Hydrotreated Product Slate^a

Hydrotreatment Run No.	N563	N566	N562	N564
Solubilization Step Temp., °C	353	353	375	375
Polishing Step Temp., °C	433	461	435	458
Gas + Water Yield	35.16	34.04	17.27	17.68
Liquid Yield				
Distillate	56.35	31.46	66.04	67.08
Soluble Resid	3.33	9.00	4.12	3.26
Oxygenates	-0.13	17.77	9.13	2.49
Total	59.55	58.23	79.29	72.83
Conversion, % maf coal fed to system	92.40	93.57	96.64	90.88

^a Yields are given as percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

TABLE 4

Comparison of Gas Plus Water Production for Task 1 Run Series^a

Hydrotreatment Run No.	N563	N566	N562	N564
Solubilization Step Temp., °C	353	353	375	375
Polishing Step Temp., °C	433	461	435	458
Pretreatment	2.00	2.00	2.00	2.00
Solubilization	17.95	17.95	8.29	8.29
Polishing				
CO ₂	4.77	5.42	2.55	4.50
C1-C3	6.77	7.62	2.91	2.75
Other	3.01	2.61	-0.21	0.15
Total Polishing	14.55	15.65	5.25	7.40
Hydrotreatment	0.66	-1.56	1.73	0.00

^a Gas + water yields are given as the percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

produced at higher polishing temperatures, but that the hydrocarbon gas (C1-C3) yield is about the same.

3.1.3 Conclusions

- As part of the integrated run sequence, solubilization (Step 2) performed at 375°C produces higher yields of better-quality hydrotreated liquid products than solubilization performed at ~353°C.
- As part of the integrated run sequence, polishing (Step 3) performed at ~435°C results in desirable liquid product slates and high conversion levels without the retrograding that was noticed at the higher polishing temperature.
- Of the run sequences tested, it would appear that a run sequence incorporating a solubilization step at 375°C and a polishing step at 435°C (i.e., a run series similar to that of N562) would produce the greatest yield of high-quality, desirable products.

3.2 FY'91-92 Task 3--Final Project Report

The final project report, covering all activities relevant to the development of the EERC multistep liquefaction process, will be prepared after all remaining studies have been completed. Funding is currently being pursued to evaluate the effect of changes in severity of the hydrotreatment step (Step 4). If the funding is approved, the task will consist of 12 autoclave tests, supporting analytical effort, and the reduction and reporting of data. It is expected that this task will require 12 months to complete following receipt of funding. The final project report will incorporate the information gathered during this task.

4.0 FUTURE OBJECTIVES

- If approved, lower-severity hydrotreatment conditions (lower temperatures and pressures, shorter residence times) will be investigated to determine their effect on the EERC's integrated liquefaction process.
- The final project report will be prepared.

13. Signature of Recipient and Date <i>[Signature]</i> 7/25/92	14. Signature of DOE Reviewing Representative and Date
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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Low-Rank Coal Direct Liquefaction (5.1)		3. Reporting Period 3-1-91 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-88	
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Task 1	Further Investigation of Pretreatment and Lower-Severity Processing:				
1.a	Batch testing	3-31-92	5-92	Changed during re-APP	
1.b	Analytical	6-30-92	6-92		
Task 2	Investigation of Cationic Pretreatment:			Task 2 deleted during re-APP	
2.a	Batch testing				
2.b	Analytical				
Task 3	Final Project Report	8-31-92			

6.0 GASIFICATION RESEARCH

6.1 Production of Hydrogen and By-Products from Coal

**CATALYTIC COAL GASIFICATION FOR HYDROGEN PRODUCTION
PILOT PLANT DATA AND SCALEUP CONSIDERATIONS**

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

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CATALYTIC COAL GASIFICATION FOR HYDROGEN PRODUCTION PILOT PLANT DATA AND SCALEUP CONSIDERATIONS

1.0 INTRODUCTION AND SUMMARY

This is the final semiannual report for a six-year program conducted by the Energy and Environmental Research Center (EERC) exploring the effects of catalytically enhanced reactivity of coals to accelerate gasification rates for the production of hydrogen and hydrogen-methane mixtures. As a companion volume (1), released concurrently with this report, a brief Executive Summary report will cover the entire project chronologically and summarize the salient conclusions. This semiannual is essentially a topical report, presenting detailed analysis of pilot-scale studies conducted over the past year, which has been cited in the preceding semiannual report (2).

The effort of the past six months has consisted primarily of analyses of earlier 1-lb/hr continuous pilot-scale tests, done in the final weeks of the preceding period, and the development of some correlations between laboratory and pilot data, leading to some cautious conclusions regarding the design of gasifiers to realize, as far as is possible, the economic advantages of catalytically enhanced coal-char gasification. This report presents this most recent experimental results in enough detail for critical scrutiny by those who wish to draw on them in support of plans for more extensive pilot efforts and commercial-scale feasibility studies.

In summary, a wealth of determinations by thermogravimetric analysis (TGA) of coal-char reactivity indicates that impressive enhancement of initial reaction rates, up to two orders of magnitude, is possible by addition of impregnated alkali catalysts. TGA is the established method of defining and comparing the reactivity of which determines the reaction rate of devolatilized char and steam to produce hydrogen. Reactivity is defined in detail in Appendix A, taken from an earlier report for a parallel project (3). Continuous pilot plant studies during the past year, in different units, at throughput rates from 1 to 40 lb/hr, have indicated more uncertainty as to the effects of catalytic enhancement of reaction rates than is apparent from TGA data alone. Correlation of TGA-defined (batch) reactivities with effective continuous process reaction rates would make TGA data far more useful as a preliminary design input.

The number and duration of both large (40 lb/hr) and small (1 to 4 lb/hr) pilot-scale tests were limited because pilot plant equipment was in various states of modification and/or in use for similar but different purposes. Notwithstanding such constraints, the data have provided significant insights as to the nature and definition of char reactivity and support some specific recommendations on the design of coal gasification systems to realize the benefits of enhanced reactivity through catalysis. In summary, these conclusions can be summarized qualitatively as follows. Their order of presentation is generally random and is not a measure of relative importance. Specific recommendations are highlighted:

- Impregnation of Wyodak coal with potassium hydroxide, at a potassium to fixed carbon ratio of around 0.2 or greater, roughly doubles the gasification reaction rate in fluidized beds of limestone. Soluble potassium, in any convenient form, is recommended as a rate-enhancing

catalyst, subject to supply costs and efficiency of recovery by leaching. This confirms earlier studies (by Exxon and others) using different coals.

- In a fluidized bed of taconite, the reaction rate enhancement by potassium impregnation appears at least as great as in a limestone bed. This was not predicted from TGA measurements, which indicate that limestone makes a small but significant contribution to reactivity, while taconite alone has essentially no rate-enhancing properties.
- Reactivity coefficients defined by continuous test results are a different but closely related property and are over an order of magnitude lower than standard TGA-determined reactivities numerically, but appear consistent in the ranking of feed-bed-catalyst conditions by reaction rate.
- The most useful result from the continuous process unit (CPU) is determination of specific capacities, defined as pounds per hour of fixed carbon converted per volume of reaction vessel. This property shows excellent correlation with CPU-derived reactivities by an empirical, exponential function, or by an approximate straight line function for the upper half of the range measured. This defines reactor volume for known sets of conditions and desired degree of fixed carbon conversion.
- The above TGA-determined reactivities of the bed content in two runs were numerically nearly identical to the corresponding specific capacity, defined above, within normal experimental scatter. In future work, if in-bed TGA-determined reactivities, in 1/hr, can be demonstrated to be essentially equal to specific capacity, in (lb/hr) per cubic foot, the direct applicability of TGA data to gasifier design will be increased tremendously, bypassing much of the more costly CPU testing. It is recommended that all future CPU and larger-scale continuous pilot runs include TGA tests of bed material, to add to an effective reactivity database.
- The CPU-determined reactivities increase consistently with temperature and are relatively insensitive to pressure, within the range studied, and steam/carbon ratio. While a limited experimental matrix covered different values of the latter two variables, differences were no greater than experimental scatter. The form of reactivity variation with temperature is consistent with that observed for TGA-determined reactivities.
- Potassium impregnation clearly enhances reaction rates, but, in a practical process, will require an efficient leaching step for potassium recovery to be economically viable. Ash-leaching studies, associated with the tests reported here, indicate that potassium recoveries over 95% can be easily achieved.
- Earlier TGA results suggest that a weight ratio of potassium to fixed carbon of roughly 0.4 will give maximum reactivity enhancement. It is believed that at this K/FC ratio active sites ($-COO^-$) on the coal structure are saturated with K^+ ions. Further increasing the K/FC

ratio results in no further rate enhancement. This is based on data for bituminous coal and wood, but has not been confirmed for lignite and subbituminous coals. It is recommended that TGA saturation test series be done on any candidate coal for catalytic gasification.

- For these CPU tests, control over the actual degree of potassium impregnation during feed impregnation proved more difficult than expected, apparently leaving a lot of the KOH catalyst free (nonion-exchanged) and subject to segregation during handling and feeding, as well as in the gasifier itself. The level of catalysis thus became another process parameter subject to random variation during the tests.
- Ash analyses and potassium balances for these tests indicated striking, consistent, but unexplained differences in the chemical state of the potassium between beds of limestone, taconite, or coal ash alone. The mobility of the potassium, and, hence, its catalytic effectiveness, appears to be substantially enhanced or limited by its reactions with other inorganic components in the bed or coal ash. This is based on presumed inorganic equilibrium, achieved over many hours at steady state, and cannot be observed by TGA data. It is recommended that future fundamental efforts in alkali catalysis include detailed studies on catalyst-mineral reactions, paralleling the level of effort at the EERC applied to equivalent reactions during combustion. Significant testing in this area can be done in the EERC's 1-lb/hr CPU.
- The fact that most of the taconite tests showed at least equal reactivities at significantly lower potassium level than the limestone tests makes taconite's equal or slightly superior performance still more impressive. Taconite is recommended as a bed material for gasifier design, site-specific supply costs permitting. Its potential for promoting methane formation or for sulfur capture is neither demonstrated nor refuted by the data reported here. In addition to at-least-equal catalytic effects, taconite is harder than limestone and should, therefore, require lower rates of bed replacement.
- Simple theoretical considerations reveal that standard TGA-determined reactivities reflect only initial slopes of generally first-order reaction curves. After longer reaction times, at reduced levels of fixed carbon, the difference in reaction rates indicated by TGA data is much less, accounting generally for the less striking reactivity differences in CPU data.
- For the above reason, design of fluid-bed (completely mixed) gasifiers requires a rapidly increasing residence volume and capital cost for increasingly complete carbon consumption. It is, therefore, recommended that overall plant designs should feed all coal, fines included, into gasifiers and use residual char for on-site boiler fuel.
- TGA tests on both feed and bed overflow product indicated that there is no significant decrease in reactivity as remaining carbon is depleted, which agrees with basic theory. This refutes a hypothesis

that the effective reactivity of a coal may reflect a composite of reactivities of different macerals within the sample.

- The CPU was operated at feed rates normally used for mild gasification (pyrolysis) testing, which resulted in generally higher levels of residual carbon than would be acceptable in a practical gasification process. This enabled more meaningful measurements of reaction rates, which was a major objective of these tests, than would be possible at near-complete carbon conversion.
- As to product gas composition, variation with pressure and steam-carbon ratio was generally less than the experimental scatter, while averages of all gas yield data showed a variation with temperature consistent with theory.
- The CPU, at 1- to 4-lb/hr capacity, represents the bare minimum scale on which gasification process evaluation can be of significant value. Due to heat losses, inaccurate gas flow measurements, and possibly irregular fluidization, experimental scatter exceeded the range of gas yield and composition variables of interest. It is recommended that any future tests on this unit should involve longer runs, multiple replications of material balance periods, and multiple samplings of all products during each in order to provide statistical credibility.
- In all gas samples, H_2S levels fell below the detectable analytical limit, precluding any observation of sulfur capture potential for the conditions studied. This is consistent with the use of low-sulfur ($S = 0.63\%$ maf) Wyodak coal.
- To augment TGA and CPU methods for feed-catalyst-condition screening, a new research tool, the integrated bench-scale gasifier (IBG) has completed preliminary shakedown testing and shows a very good possibility of essentially replicating TGA data on a larger scale, of 200-300 grams, as compared with 20-50 milligrams for the TGA. Unlike TGA, this unit can provide samples of residual char and condensable liquid coproducts large enough for complete analysis, and multiple or replicate gas samples. Extensive use of this unit is presently scheduled for two related projects.
- Data from the last successful, weeklong run by EERC's continuous 40-lb/hr process demonstration unit (PDU), for Wyodak coal in a bed of limestone, were reviewed for comparison with the CPU data reported here. Specific capacity data, lb of fixed carbon converted per hour, per cubic foot of reactor volume, were over twice as great for the PDU as for the CPU, establishing the CPU data as a conservative basis for preliminary gasifier design.
- It must not be forgotten that process heat for the CDU is provided electrically, so that gas yields and concentrations of hydrogen or methane are unrealistically high. Future interpretation of CPU data should include calculation of the amount of additional coal that would be consumed to supply process heat in a real-world gasifier, assuming various heat utilization efficiencies.

- Results from this and parallel studies are still inconclusive regarding the potential use of sodium as an economical alternative to potassium as a gasification catalyst. Large PDU-scale tests are needed to determine whether preimpregnation of sodium or potassium on feed coal, as homogeneous catalysts, will result in the agglomeration problems observed with heterogeneous (cofed) trona and nahcolite earlier in this project. Because of the very small bed size, the CPU is not recommended for studying mechanical factors affecting bed fluidization.
- For firm engineering design data and identification of operating problems, future pilot plant efforts should be done on a significantly bigger capacity scale than the EERC PDU system described here. Such a facility must be built for and dedicated to the single purpose of hydrogen/methane production, on a budgetary scale large enough to ensure complete shakedown operation and extended runs of at least a week on each set of conditions considered, with several replications of all runs showing promise for commercial-scale designs.
- EERC has on hand nearly all the components to assemble a substantially larger pilot gasifier system than the PDU used in this project. The vessel, partial feed system, and gas cleanup train may be suitable for up to twenty times the PDU capacity at near ambient pressures, with further increases possible at pressures to possibly 35 atmospheres. The vessel is large enough to accommodate multiple bed and feed configurations.
- As an alternative approach to further process development, small demonstration gasification projects should be considered, preferably integrated with utility plants to minimize capital and fixed operating costs of facilities and auxiliary systems. If/when such a system is in operation, relatively inexpensive tasks would be to vary the bed material and impregnate batches of feed coal, for several weeks of operation, with potassium or other catalysts. The first step along this route would consist of site-specific feasibility studies to establish the costs and benefits of such demonstration plants.

2.0 BACKGROUND

Since the mid-1970s, the United States has been in a state of apprehension over the next energy crisis and in eager anticipation of the next generation of energy supplies. While still unresolved, it appears reasonably certain that, for decades to come, the U.S. will, or should, rely increasingly on coal, simply because it is cheap, and we have an abundance of it. It is also apparent that somewhere within the continually shifting, multiple scenarios predicted, there will be an expanded market for hydrogen, either as an end product or an essential intermediate. This observation is summarized in Figure 1, showing the full array of potential markets for hydrogen from coal. The most economically proven source of hydrogen is reformation of natural gas, itself a valuable commodity and of potentially limited supply. In any scenario of complete energy independence, natural gas is too ideal a fuel for domestic heating and short-term emergency utility and industrial uses to deplete for massive hydrogen production for any extended (multidecade) period. Efficient electrolytic hydrogen production using wind or solar power

is still decades of development away from economic feasibility. Therefore, any medium-term policy to significantly accelerate commercial production for the markets noted in Figure 1 must depend upon coal. In order for the potential of coal as a hydrogen source to be realized, valid process data must be generated, from which process options and gasifier designs of maximum yield and minimum capital and production cost can be identified.

The emphasis of this project has been on the effects of catalysis, to reduce reaction severity and reduce capital costs, with gasifier and process design of interest only to realize on a practical scale the benefits of catalysis as indicated by TGA data. As an overall program rationale, the increasing scale of catalyst screening at the EERC, in terms of size and research cost, is indicated by Figure 2. TGA screening is well established as a standard evaluation tool, is relatively inexpensive, and has provided most of the useful data to date, indicating the substantial increases in the reaction rate between coal char and steam to produce hydrogen that are possible through catalysis. The IBG (integrated bench-scale gasifier) system allows larger-scale batch testing, providing gas, solid, and liquid product samples large enough for thorough analyses. This device was completed too recently to generate significant data within the funded period of this project, although some shakedown tests will be discussed briefly in this report, to demonstrate its potential as a research tool.

The CPU (continuous process unit) system is a minimum-scale, "near-simulation" of continuous, fluid-bed process conditions, falling short of achieving full-scale process conditions only in that it is externally (electrically) heated, so that product gases are unrealistically rich, being undiluted by the CO_2 from the burning of extra feed to provide internal process heat. Most of the data presented in this report were generated by CPU tests. This unit was designed primarily for char production (mild gasification), rather than for complete gasification, somewhat limiting its usefulness. However, the incomplete consumption of char, in effect, allowed study of the catalyzed gasification reactions under conditions of varying carbon levels in the fluidized bed. Finally, the PDU (process demonstration unit) is a complete process simulation, capable of generating process engineering data and realistic material balances for selected process conditions.

Earlier in this project, the PDU was operated successfully, generating an array of useful data, until it was shut down, modified, and semi-integrated into pilot facilities for mild gasification and pressurized fluid-bed combustion. Following this renovation, a substantial amount of time and funding was required to bring the unit to full operational status. Consequently, there was little useful, steady-state data on catalytic steam gasification, and scheduled runs were scaled down to the CPU level, producing most of the conclusions of this report. (As a note on nomenclature, the PDU and CPU definitions apply to this report and EERC work during the past two years. Some earlier EERC reports (4) refer to the 40-lb/hr unit as a CPU.)

By way of broader background, some earlier PDU data and some proposed plant design concepts from this and parallel projects will be discussed, relative to the conclusions drawn from the data presented here. Detailed TGA and prer renovation PDU results have been published earlier (4,5), as well as has a marketing study of commercial hydrogen from a hypothetical, commercial-

Figure 1. Emerging markets for hydrogen from coal.

Figure 2. Scaled gasification capabilities at the EERC.

scale plant (6). The PDU data were used as the basis for an outside subcontractor, Black and Veatch (B&V), to do an engineering feasibility study (7) based on the best available set of PDU operating data. That study assumed a straightforward, though inefficient, gasification process design, with alternatives for hydrogen, methanol, or electricity via fuel cells as the end products. That study assumed a western subbituminous coal in a limestone bed, with no other catalyst. An earlier, definitive study by Exxon (8) considered a process using an eastern bituminous coal, catalyzed by potassium impregnation, to produce a gas high in both hydrogen and methane, followed by shift conversion for methane (synthetic natural gas) production. An ongoing, parallel study by the EERC (experimental) and Fluor-Daniel Engineers (F-D), under subcontract to Energy Research Corporation (ERC), assumes an eastern bituminous coal to produce hydrogen-methane mixtures for advanced fuel cells, which, in turn, may produce electricity at overall efficiencies approaching

60%. This study has also addressed the use of potassium-impregnated bituminous coal. It has so far produced a multioption engineering cost study (9), by F-D, assuming the same bituminous coal (Illinois No. 6) in a limestone bed. Though beyond the scope and budget of this report, these studies should be reviewed in the light of the experimental conclusions reported.

3.0 OBJECTIVES

3.1 Project Objectives

The broadly defined objectives of this report are as follows:

- To determine gasifier operating conditions and catalyst selections to maximize the production of hydrogen, methane, condensible products, marketable char and activated carbon
- To develop kinetic models, based on empirical data, to predict product yields under real-world conditions
- To explore the potential for in-bed sulfur capture by selection of bed and catalyst material
- To apply the above objectives primarily to lignite and subbituminous coals, with extensions to bituminous coals where convenient

3.2 Process and Plant Design Objectives

All indications are that significant enhancement of throughput capacity, and possibly of hydrogen and methane yields is possible by catalysis, but is of little practical utility until reflected in viable commercial-scale plant designs. Any process design, even a preliminary one for rough economic feasibility evaluation, must assume the best selection possible of catalysts and design of a gasifier to realize the maximum advantages indicated by experimental data available, however marginal or incomplete. While the data reported here are not sufficient as a basis for reliable gasifier plant designs, they are reported with the plant design application in mind to assist those interested in the practical (economic) application.

3.3 Report Objectives

With the completion of this project, the goal of this report is to extract the maximum useful content from the recent pilot-scale data at the EERC, both from the viewpoint of preliminary process design and of fundamental understanding of the kinetics of steam-coal reactions in a fluidized-bed environment. A secondary goal is to preserve, through documentation and the discussion of data, the various "loose ends" of unanswered questions, to be addressed in any follow-on efforts.

4.0 THEORETICAL: BATCH AND CONTINUOUS REACTIVITIES

The overall purpose of this project has been to identify catalysts to substantially enhance the reactivity of coals and to improve gasifier efficiency, through lower reaction severity, for the production of hydrogen

and methane. Thermogravimetric analysis (TGA), on which the definition and measurement of reactivity is based, has demonstrated that coal reactivity can be increased by as much as two orders of magnitude by the proper selection of catalysts. A detailed definition of reactivity and a description of how it is measured (3) is included as Appendix A. Table 1 shows an array of standard reactivities for a variety of coals, with and without various catalysts, from TGA tests at the EERC over the past seven years, done under a number of different projects. The salient conclusion from these data is that low-rank coals (lignites and subbituminous) are more reactive than high-rank (bituminous) coals and that the use of some catalysts greatly enhances the native or intrinsic reactivity. To be of practical value, it is essential to predict to what extent this enhanced reactivity of all ranks of coal may be achieved in continuous gasifiers.

For TGA data to be truly relevant to catalyst evaluation, it is essential to determine the degree to which TGA-determined reactivities can be correlated with measured reaction rates in continuous systems.

The dominant reaction in coal gasification, whose rate determines the overall rate of conversion to gases, is the steam-char reaction:
 $C + 2H_2O \rightarrow 2H_2 + CO_2$. "C" in this case refers to the nonvolatile carbon, which is approximated by the fixed carbon, FC, as reported in the standard proximate analysis, which is the variable actually measured during standard TGA tests. The larger weight of total carbon, as reported in a standard ultimate analyses, is not used here, since the difference is included in the volatile fraction, which pyrolyses quite rapidly at gasification temperatures. The overall rate of carbon consumption is dominated by the slower steam-char or steam-carbon reaction. This reaction can usually be represented by a first-order reaction rate, which is determined by the differential equation:

$$-(dC/dt) = k_0 C^n$$

and its exponential solution, for $n = 1$, which is:

$$C(t) = C(0) e^{-k_0 t}$$

where $C(t)$ is the amount of fixed carbon in the reaction zone at any time, t , in hours. The exponent, n , is the reaction order, generally assumed equal to 1 as a simplifying approximation. The initial weight of carbon, not a weight or mol fraction, is defined as $C(0)$, at $t = 0$. In a batch reaction, such as the TGA analysis, at the moment the reaction starts, the rate or slope of carbon decrease is at its maximum:

$$dC/dt = -k_0 C, \text{ or } C(t) = C(0) - k_0 t, \text{ at } C(t) \rightarrow 0$$

and decreases as the carbon is consumed, much like a fire dying down. In a standard TGA analyses, the approximate or standard reactivity, k , with no subscript, is defined as the average rate of the first 50% of the carbon consumed. Figure 3 shows a normalized exponential curve, $C(t)$, for an arbitrarily assumed value of $k_0 = 2.0$, the initial slope, $-k_0 t$, and a tangent line, representing the reduced rate of carbon loss when $C = 50\%$. Added to these is a hypothetical straight line, connecting the initial (100%) and the 50% points, which is used to define standard reactivity, k . Note that it shows a slope intermediate between the absolute or true reactivity, k_0 , and

TABLE 1
Reactivities (K, 1/hr) of Raw and Catalyzed Coals
by Thermogravimetric Analysis

Temperature, °C		650	700	750	800
Velva (ND) Lignite					
No Catalyst		0.30	1.35	2.10	3.55
10% K ₂ CO ₃		1.35	4.06	8.17	34.80
10% Trona (Na ₂ CO ₃)		1.92	6.05	16.46	
10% Limestone		0.48	0.81	6.49	15.50
20% Limestone		0.55	5.00	8.76	15.00
10% Taconite			1.33	1.63	2.85
10% Taconite, 4% Trona			3.56	8.46	
Wyodak (WY) Subbituminous					
No Catalyst	a*	0.37	1.16	1.31	3.05
10% K ₂ CO ₃	a	1.25	4.30	8.24	13.48
10% Trona, 10% Taconite	a		1.00	3.33	7.65
No Catalyst	b		0.70	1.20	2.70
10% K ₂ CO ₃	b		4.00	5.20	7.20
No Catalyst	c			2.34	
2.8% K	c			2.81	
5.6% K	c			2.86	
8.4% K	c			4.74	
11.2% K	c			4.55	
14.0% K	c			5.67	
15.8% K	c			7.93	
No Catalyst	d		0.84	0.94	2.23
10% K ₂ CO ₃	d		9.87	11.13	13.07
No Catalyst	e		1.33	3.28	7.33
Limestone	e		1.26	3.01	3.86
CaO (6% Ca ⁺⁺)	e		3.80	6.36	15.74
CaSO ₄ (6% Ca ⁺⁺)	e			2.77	
Ca(C ₂ H ₃ O ₂) ₂ (6% Ca ⁺⁺)	e			4.55	
Illinois #6 Bituminous					
No Catalyst			0.07	0.14	0.33
10% K ₂ CO ₃				4.36	
10% Wood Ash, Cold Leach.			0.95	2.60	8.54
10% Wood Ash, Hot Leach.			0.61	3.01	5.15
20% Limestone				0.59	1.45
20% Dolomite				0.25	0.90
18% Limestone, 2% K ₂ CO ₃				0.36	
15% Limestone, 5% K ₂ CO ₃				0.89	
12.6% Limestone, 7.4% K ₂ CO ₃				3.55	
10% Limestone, 10% K ₂ CO ₃				5.38	
15% Taconite, 5% K ₂ CO ₃				0.15	
10% Taconite, 10% K ₂ CO ₃				4.97	
5% Taconite, 15% K ₂ CO ₃				4.17	
Indiana Bituminous					
No Catalyst			0.18	0.16	0.31
CaO (6% Ca ⁺⁺)			0.21	0.58	1.26
CaSO ₄ (6% Ca ⁺⁺)			0.17	0.32	1.17
Ca(C ₂ H ₃ O ₂) ₂ (6% Ca ⁺⁺)				0.66	

* a-e indicate test series on five different Wyodak coals, some from different mines, indicating variation in coal type.

Figure 3. Standard and "true" reactivities for steam-char reaction.

50% tangent line. In a typical set of TGA data, the distinction between the k line, the k_0 line, and the exponential curve is generally not obvious in this range, due to the combined effects of experimental scatter and minor deviations from first-order behavior. The standard definition of reactivity, k , without subscript, is thus based on this easy-to-read line on experimental data plots, such as the several examples shown in Appendix A.

Throughout this study, analyses of data assume first-order behavior. TGA data indicate, however, that heavily alkali-catalyzed reactions tend to have lower order reactivities, with $n < 1.0$, which results in a faster $-dC/dt$, which tends less to slow down as carbon is depleted. In this respect, all conclusions that can be drawn from this work, regarding throughput or gasifier size, will err on the conservative side. Real-world reaction rates are thus expected to be a bit faster.

To relate the TGA-derived, standard reactivity, k , to the absolute reactivity, k_0 , note that k is the slope of a straight line $= 50/t_{50}$, where $t_{50} = -\ln(0.5)/(-k_0)$ is the time at which $C(t) = 50\%$. By rearranging the normalized exponential function above and setting $C(0) = 1$, $k = 0.7215k_0$ or $k_0 = 1.386k$. This difference is relatively insignificant, compared with the differences in reactivity with temperature and for different coals and catalysts, shown in Table 1.

Returning to Figure 3, the 50% tangent line roughly represents the reaction rate that the hypothetical coal or char is experiencing when it is 50% depleted by the reaction. Consider next a fluidized-bed gasifier, with a continuous bed overflow, as is the case of the continuous process unit

described below. If the overflow, at steady-state conditions, contains 50% of the fixed carbon entering the system, it may be valid to say that this slope dC/dt , determined by a material balance, equals the reaction rate at $C = 50\%$. Recombined as the above differential equation, the reactivity might be reconstructed as:

$$k = -0.7215 (dC/dT)/C$$

which, by definition, should be valid for any value of C as the amount of carbon remaining. Therefore, if such a reactor is sized to achieve 95% carbon (FC) conversion, the average or effective reaction rate would be the slope at $C(t) = 0.05$, shown as a straight line, starting at the origin, near the top of Figure 3. This would clearly apply in the case of a plug flow reactor, at its discharge (top) end, with the higher k_0 value at its bottom end. However, if a fluidized-bed reactor is assumed completely mixed, the overflow will be a mixture of particles that have been in the reactor for very different lengths of time, each representing a degree of depletion at different points along the $C(t)$ curve. Therefore, it must be emphasized that the easily measured "reactivity" in a continuously and presumably completely mixed reactor is not the same parameter as that measured by the standard TGA test. So let us hereby define the "continuous reactivity" as:

$$k_c = (dC/dt)/C$$

where C is the fraction of the amount (kg or lb) of fixed carbon content in the reactor bed, determined by analysis of the bed overflow stream, leaving the system unreacted. With this assumption, the choice of units is consistent with that of the definitive equation assumed in TGA analyses, $(\text{kg/hr})/\text{kg} = 1/\text{hr}$, where both weights can be expressed on a per volume basis for gasifier scaling studies. C must not be confused with simply the FC content (%) of the reactor bed, which is often higher than that of the feed stream, due to rapid loss of the carbon in volatiles.

If we plot the exponential function $C(t) = 100 e^{-k_0 t}$ for different values of k_0 , or k , the advantages of increased reactivity are fairly obvious, as shown by the examples in Appendix A, many of which appear to be straight lines down to fairly low levels of residual carbon, indicating less than first-order reaction; that is, $n < 1$ in the more general equation. If we assume first-order behavior, however, and extend all $C(t)$ curves to 90% completion, we note that the slopes of the high- k curves are eventually less than those of the low- k curves. In Figure 4, using the general equation, $C(t) = 100 e^{-k_0 t}$, the derivatives, dC/dt , are plotted against time. Note that, notwithstanding the great difference in initial rates, the ranking of reaction rates is eventually reversed. In other words, assuming first-order behavior to apply, the longer a unit charge of carbon is retained in a reaction zone to achieve near-complete conversion, the less are the advantages of an enhanced reactivity. Such long residence times, however, will generally be beyond those of any commercial significance.

As a less simplistic model of reactivity, for specific sets of reactivity data, the actual or calculated reaction rate which is also normally reported becomes more significant. See Appendix A for a more thorough discussion of calculated, as opposed to assumed, first-order reactivities.

Figure 4. Reaction rates vs. time for different k values.

In a completely mixed, fluidized-bed reactor, with a low and uniform residual carbon level, there arises a question of how much difference a greatly enhanced reactivity, k , can make in throughput capacity. This question will be addressed further in a later section, in the analysis of experimental data.

There also arises the question of how and whether a k_c from a continuous reactor can be mathematically related to a k_p from TGA results. It is tempting, referring to Figure 3, to add another line, from the 100% origin to some $C(x)$, $t(x)$ point along the curve, where $C(x)$ is the amount of carbon in a reactor bed at time $t(x)$, which might be the average time in the bed of all reacting particles. Defining the slope of such a line as k_c further defines a fictitious C_0 point at which $C(t) = 100\%$ at $t = 0$. This would be the initial weight of carbon in the reactor bed if it had been a batch reaction at an unknown k_0 , defining a first-order function passing through $C(x)$, $t(x)$. This assumption now defines the following two equations:

$$C(x) = C_0 e^{-k_0 t}$$

$$k_c = (C_0 - C(x))/t(x)$$

Unfortunately, these two equations contain three unknowns: C_0 , k_0 , and $t(x)$ and, therefore, appear unsolvable. Clearly, any other-than-empirical $k_0 = f(k_c)$ function would be valuable in predicting continuous process behavior from the far cheaper TGA data and warrants further investigation.

5.0 CONTINUOUS PROCESS UNIT

5.1 Apparatus and Experimental Procedure

EERC's continuous process unit is shown schematically in Figure 5. A mixture of sized coal, bed makeup, and catalyst is fed from the pressurized feed hopper through a precalibrated feed auger. The feed hopper is weighed at the beginning and end of mass balance periods. Water is fed to an electric boiler/superheater by an accurate metering pump. Nitrogen is metered in by a rotameter, backed up by weighings of the source cylinder. The system is rated for about 150 psig, although operation at this pressure was limited by the capacity of the solid feed system and minor leakage problems. All vapors are cooled and condensed in stages. Solid and liquid products are collected and weighed as often as collection pots fill up and at the end of each material balance period. Not shown in Figure 5 are several dozen thermocouples, by which temperatures throughout the system are monitored continuously. All solid feeds and product samples are available for proximate and ultimate analyses and x-ray fluorescence analyses of their ash components. A run is defined as at least a 4-hour material balance period, after steady-state operation has been achieved, which may take eight or more hours.

The combined gas flow, following condensation of nearly all water and liquid organic products, is metered through a continuous displacement gas meter of limited accuracy. A gas bag sample is taken at least once per balance period for analysis by gas chromatography (GC). A preliminary material balance is done, using standard software developed by EERC's mild gasification project. Printouts are included in Appendix B. Cumulative inaccuracies in gas flow measurements show up here as deviation from a perfect closure on the nitrogen balance. All exit gas flows, based on GC analyses, are adjusted in the same proportion until the nitrogen balance shows a 100% closure, assuming the accuracy of the nitrogen feed measurement.

The component gases are then normalized and reported on a dry, inert-free basis. This and all analyses are then fed into a graphic, "user-friendly" data reduction program composed for this project, for which an example is included as Appendix B, along with summary sheets for all seventeen runs reported here. Data for each run are then stored on disk for later, detailed analyses.

The analyses of blended feeds for these series of tests are shown in Table 2. An initial objective was to apply the KOH catalyst intimately onto the coal in a ratio of about 0.12 mols of potassium per mol of FC (fixed carbon), determined by proximate analysis. This was done by dissolving pellets of 87% KOH in minimal water, mixing with the raw coal, and then redrying. The final, as-fed blends of raw or impregnated coal were then analyzed. It is now suspected that substantial amounts of the KOH did not undergo ion exchange with the coal and were present only as a surface deposition, allowing it to separate during grinding, thus causing the wide differences in K/FC mol ratios in Table 2 and in reactor bed analyses reported later.

When the system is started up, gas, solid, and condensate products are sampled and weighed through several complete change-outs of the reactor vessel, until repeatable weights, as well as constant temperatures, pressures

Figure 5. EERC's continuous process unit.

and flow rates, suggest that steady state is achieved. This normally requires at least eight hours. All product collection pots are then emptied, and a standard, 4-hour material balance period is started. Solid products are collected and analyzed for both the bed overflow and the cyclone, shown in Figure 5. The distribution and analysis of the two solid samples provide the primary measure of the degree of completeness of the reaction and the extent of carryover, which, in turn, indicates whether fluidization velocity was adequate or excessive. Screen analyses of the bed and cyclone solids would also indicate the degree of attrition and required bed makeup rate. In this series, however, the bed was fed at a high rate, ensuring substantial bed overflow so that a significant amount of unreacted carbon could provide some indication of the reactivity at the conditions covered.

Solid and gas samples, to be analyzed after the run, are normally taken at a time late in the 4-hour material balance period. In the first seven tests reported here, two or three sets of solid and gas samples were taken, about two hours apart, and analyzed separately to indicate the range of variation during the material balance period. This procedure was not continued through the entire series, however, in the interest of economy.

5.2 Experimental Objectives and Rationale

The intent of these experiments was to go through a minimal array of temperatures, pressures, and steam-carbon ratios for steam gasification of Wyodak coal, impregnated with potassium hydroxide, in fluidized beds of limestone and taconite. A bed makeup rate of 20% limestone or taconite is assumed. A short initial series of four runs used raw Wyodak coal and limestone, without potassium impregnation, as a basis of comparison. Earlier TGA data (2) establishes that limestone alone is a cheap, moderately effective catalyst; that taconite alone has essentially no catalytic effect; and that reactivity enhancement by KOH impregnation is substantially greater than the difference between limestone and taconite. Taconite is also of interest for its possible promotion of the methanation reaction and as a possible sulfur-capture agent in the 600°-650°C range, at which, in combination with higher pressures, methane production is favored. The temperature range selected for these tests, 600° to 700°C, is below the range known to offer good gasification rates, but was selected to best observe the effects of catalysis, in terms of both increased methane yields and the potential economy of operation at lower temperatures.

An experimental matrix consisted of tests at temperatures of 600°, 650°, and 700°C for the cases of K-impregnated coal, with a few digressions to higher pressures and steam/carbon ratios. For comparison, four tests were done with raw coal in a limestone bed, which was the basic operating condition used in earlier PDU tests (5) and which was the basis for subsequent engineering and cost study (9).

5.3 Summary of Data

Complete printouts of data for two runs are presented in Appendix B, while summaries for all runs are covered in Tables 3-A, 3-B, and 3-C for the cases of raw-coal-plus-limestone, impregnated-coal-plus-limestone, and impregnated-coal-plus-taconite, respectively. The definition of these

TABLE 2
CPU Feed Analysis

Run Nos.	Raw Coal	M-216-220	M-221-227	M-228-234
Bed Makeup	---	Limestone	Limestone	Taconite
% of Feed	---	20.0	20.0	22.5
Impregnated Catalyst*	---	None	KOH	KOH
Proximate %				
Moisture	28.60	21.30	20.70	20.70
Dry Basis				
Volatiles	45.29	48.40	46.32	39.22
Fix Carbon (FC)	47.84	35.20	28.70	28.50
Ash	6.87	16.40	24.98	32.28
Ultimate (MAF), %**				
Hydrogen	5.10	4.63	3.82	3.55
Carbon	73.49	67.94	64.00	48.51
Nitrogen	0.91	0.85	0.82	0.64
Sulfur	0.63	0.16	0.42	0.44
Oxygen	19.84	36.40	30.89	14.56
XRFA, % of Ash				
SiO ₂	25.90	7.68	12.60	47.50
Al ₂ O ₃	13.90	4.57	8.20	3.52
Fe ₂ O ₃	7.36	3.14	4.50	28.00
CaO	24.30	73.30	12.00	4.99
MgO	8.90	4.77	4.50	2.17
Na ₂ O	2.07	0.35	0.90	0.37
K ₂ O	0.35	0.53	47.70	8.87
SO ₃	15.40	5.25	8.70	4.38
Other	1.82	0.41	0.90	0.20
Mol-Equivalents/Mol FC*				
K ⁺	0.00	0.00	0.17	0.04
Ca ⁺⁺	0.05	0.49	0.15	0.08
Fe ⁺⁺⁺	0.01	0.02	0.05	0.44

* Based on analyses of coal-catalyst-bed mixtures, as fed.

** Variation in ultimate analysis reflects interaction of coal's carboxyl (-COO⁺) and other organic functionalities with mobile inorganics of limestone, taconite, and/or KOH.

variables is self-evident. They are discussed and trends identified in the following section.

Table 4, subdivided into three corresponding sections, compares reliability factors suggested as predictions of the data's validity. For the first seven runs, where double sampling was done, these factors include rates of change in hydrogen content of product gas, and of fixed carbon and volatiles in both the bed overflow and cyclone solid products, all expressed as percent change during the 2-hour interval between samples. Where this variation is greater than 10%/2 hours, the data are identified as flawed by

TABLE 3-A
CPU Run Summary
Bed: Limestone
Other Catalyst: None

Run No. M-	216	217	218	220
Run Specifications				
Temperature, °C	700.0	600.0	700.0	700.0
Pressure, atm	2.4	2.4	6.1	2.4
Feed, lb/hr	1.8	1.8	1.8	1.8
lb maf/hr	1.21	1.21	1.21	1.2
Steam/Carbon Mol Ratio	2.57	2.65	2.4	1.72
Process Response Factors				
FC Consumed, %	17.88	34.97	55.23	55.13
maf Consumed, %	40.39	54.97	64.61	63.33
Prod. Gas (Dry, N ₂ -free)				
% H ₂	56.75	46.13	62.58	58.58
% CH ₄	7.70	18.75	6.54	7.96
% CO	6.01	4.48	0.65	8.16
% CO ₂	29.29	30.35	26.94	24.99
% Other	0.25	0.29	0.35	0.31
Rate, scfh	22.50	8.98	21.50	21.35
Wt. Gas/maf Feed	0.82	0.35	0.66	0.72
Wt. Gas/FC Consumed	9.07	2.01	2.38	2.60
Wt. H ₂ /maf Feed	0.05	0.02	0.06	0.05
Wt. H ₂ /FC Consumed	0.61	0.10	0.21	0.19
Wt. CH ₄ /maf Feed	0.06	0.06	0.05	0.06
Wt. CH ₄ /FC Consumed	0.66	0.32	0.17	0.21
Cyclone Fines, lb/hr				
% Volatiles	29.93	32.99	31.57	27.32
% FC	43.29	42.79	40.17	49.00
% Ash	26.79	24.23	28.29	23.67
maf, % of maf Feed	5.40	6.33	6.57	6.27
Bed Overflow, lb/hr				
% Volatiles	34.43	27.91	31.73	30.78
% FC	27.99	44.37	35.44	30.05
% Ash	38.08	26.73	32.84	34.19
maf, % of maf Feed	65.90	47.53	35.75	37.60

TABLE 3-B

CPU Run Summary
 Bed: Limestone
 Other Catalyst: KOH Impregnation

Run No. M-	221	222	223	224	225	226	227
Run Specifications							
Temperature, °C	700	600	700	700	650	650	600
Pressure, atm	2.4	2.4	2.4	6.1	2.4	2.4	2.4
Feed, lb/hr	1.8	1.8	1.8	1.8	1.8	1.8	1.8
lb maf/hr	1.03	1.03	1.03	1.02	1.03	1.03	1.03
Steam/Carbon Mol Ratio	2.41	2.73	1.45	2.3	2.56	1.09	1.17
Process Response Factors							
FC Consumed, %	75.52	21.36	68.22	69.43	54.83	45.66	29.37
maf Consumed, %	65.20	33.18	62.09	64.70	62.90	62.87	54.98
Prod. Gas (Dry N ₂ -free)							
% H ₂	63.12	59.96	56.19	63.86	60.43	60.86	56.67
% CH ₄	2.72	9.00	7.45	6.25	5.67	6.01	9.55
% CO	8.68	2.07	16.56	5.33	6.54	6.36	3.68
% CO ₂	25.44	28.69	19.59	24.57	56.56	25.86	29.73
% Other	0.04	0.29	0.21	0.00	0.80	0.91	0.39
Rate, scfh	32.28	10.60	24.90	27.73	18.48	18.05	12.05
Wt. Gas/maf Feed	1.25	0.43	0.98	1.02	0.74	0.71	0.51
Wt. Gas/FC Consumed	2.86	3.46	2.49	2.88	2.64	3.05	3.42
Wt. H ₂ /maf Feed	0.10	0.03	0.07	0.09	0.06	0.06	0.03
Wt. H ₂ /FC Consumed	0.24	0.26	0.18	0.25	0.20	0.24	0.24
Wt. CH ₄ /maf Feed	0.04	0.04	0.07	0.07	0.04	0.04	0.05
Wt. CH ₄ /FC Consumed	0.08	0.31	0.19	0.20	0.15	0.09	0.31
Cyclone Fines, lb/hr	0.11	0.10	0.11	0.10	0.09	0.08	0.09
% Volatiles	35.66	37.21	33.40	38.27	36.90	34.80	26.80
% FC	20.48	21.04	22.80	17.35	22.00	33.96	40.20
% Ash	43.87	41.76	43.50	44.38	41.10	41.20	33.00
maf, % of maf Feed	5.74	5.52	5.99	5.43	5.16	4.58	5.87
Bed Overflow, lb/hr	0.63	0.88	0.68	0.77	0.74	0.71	0.83
% Volatiles	36.39	33.25	33.30	36.90	32.20	27.60	26.80
% FC	19.48	50.84	24.10	18.50	29.30	37.40	40.20
% Ash	44.09	32.66	42.60	44.70	38.50	34.90	33.00
maf, % of maf Feed	34.49	71.71	37.83	41.62	44.30	44.92	54.14

TABLE 3-C

CPU Run Summary
 Bed: Taconite
 Other Catalyst: KOH Impregnation

Run No. M-	228	229	230	231	233	234
Run Specifications						
Temperature, °C	600	700	600	700	650	650.0
Pressure, atm	2.4	2.4	2.4	2.4	2.4	2.4
Feed, lb/hr	1.8	1.8	1.8	1.8	1.8	1.8
lb maf/hr	1.02	0.95	0.95	0.95	0.95	0.95
Steam/Carbon Mol Ratio	1.03	1.81	2.07	1.16	2.11	1.04
Process Response Factors						
FC Consumed, %	62.89	80.83	57.07	71.60	58.63	50.13
maf Consumed, %	67.92	78.62	68.25	77.90	71.12	67.33
Prod. Gas (Dry, N ₂ -free)						
% H ₂	57.03	61.50	60.13	59.48	60.10	60.40
% CH ₄	8.61	3.71	6.90	4.36	5.90	6.10
% CO	2.47	8.52	2.03	10.81	4.20	4.90
% CO ₂	31.61	25.79	30.61	24.84	28.70	27.00
% Other	0.28	0.48	0.28	0.50	1.10	1.60
Rate, scfh	9.98	35.00	11.85	13.35	20.33	17.98
Wt. Gas/maf Feed	0.47	1.50	0.53	0.58	0.90	0.78
Wt. Gas/FC Consumed	1.20	2.99	1.50	1.31	2.40	2.50
Wt. H ₂ /maf Feed	0.03	0.12	0.04	0.04	0.07	0.06
Wt. H ₂ /FC Consumed	0.08	0.23	0.11	0.10	0.08	0.19
Wt. CH ₄ /maf feed	0.04	0.06	0.04	0.03	0.05	0.05
Wt. CH ₄ /FC Consumed	0.10	0.11	0.10	0.06	0.14	0.15
Cyclone Fines, lb/hr	0.20	0.22	0.19	0.16	0.18	0.17
% Volatiles	17.70	14.50	21.00	20.65	18.40	17.60
% FC	0.99	1.16	0.27	0.81	1.82	0.86
% Ash	81.30	81.40	78.80	78.54	74.76	81.52
maf, % of maf Feed	3.90	4.32	4.30	3.64	3.78	3.26
	1.12	0.75	0.88	0.66	0.79	0.87
Bed Overflow, lb/hr	17.50	19.70	17.20	16.35	16.20	15.50
% Volatiles	19.40	14.70	28.70	25.23	30.46	33.70
% FC	63.10	65.50	59.10	58.92	53.50	50.80
% Ash	51.77	27.22	42.53	28.83	38.82	44.92
maf, % of maf Feed						

TABLE 4
Data Reliability Factors

A. Bed: Limestone Other Catalyst: None							
Run No. M-	216	217	218	220			
Input N ₂ Accounted for	140	119	100	90			
Input H ₂ O Accounted for	78	88	50	64			
Input Ash Accounted for	140	100	102	118			
Input Carbon Accounted for	106	75	69	76			
Input maf Accounted for	112	109	107	107			
Number of Gas Samples	2	2	1	2			
H ₂ Variation (1) %	2.4	7.5	---	-1.0			
Cyclone Ash Samples	2	2	3	2			
Volume Variation, %	-5.6	3.4	0.2	-2.6			
FC Variation, %	4.6	-2.6	-2.2	1.8			
Bed Overflow Samples	2	2	3	2			
Volume Variation, %	8.9	0.7	1.4	1.5			
FC Variation, %	-20.4	-0.6	1.7	-12.7			
Flawed Data? (2)	NSS/BMB	---	---	---			
B. Bed: Limestone Other Catalyst: KOH Impregnation							
Run No. M-	221	222	223	224	225	226	227
Input N ₂ Accounted for	99	108	102	112	113	111	110
Input H ₂ O Accounted for	78	63	42	65	81	70	91
Input Ash Accounted for	95	108	98	114	94	82	89
Input Carbon Accounted for	71	91	87	95	92	92	97
Input maf Accounted for	105	110	106	112	112	112	115
Number of Gas Samples	1	2	2	2	2	2	2
H ₂ Variation, %	---	0.1	-2.2	-0.6	-0.4	0.9	-0.4
Cyclone Ash Samples	2	2	2	2	2	2	1
Volume Variation, %	-0.4	1.0	3.6	8.2	-0.6	1.2	---
FC Variation, %	-5.0	-1.3	-4.2	-35.9	-95.0	-1.1	---
Bed Overflow Samples	2	2	2	1	1	1	1
Volume Variation, #	-17.1	-60.4	-1.1	---	---	---	---
FC Variation, %	15.7	-1.2	-0.1	---	---	---	---
Flawed Data? (2)	---	---	---	NSS	NSS	---	---
C. Bed: Taconite* Other Catalyst: KOH Impregnation							
Run No. M-	228	229	230	231	233	234	
Input N ₂ Accounted for	112	109	108	215	111	111	
Input H ₂ O Accounted for	93	77	74	61	83	85	
Input Ash Accounted for	191	149	139	113	125	128	
Input Carbon Accounted for	20	67	23	67	94	96	
Input maf Accounted for	124	110	115	110	114	116	
Number of Gas Samples	2	2	2	2	1	1	
H ₂ Variation, %	1.0	-0.6	2.5	0.2	---	---	
Flawed Data? (2)	BMB	---	---	BMB	---	---	

* Only one set of solid samples per run in taconite series.

"NSS," for nonsteady state. In all 17 runs, material balance closures for nitrogen, water, ash, total carbon, and MAF (moisture- and ash-free) feed are indicated. An ideal material balance closure is 100%. Where deviation is greater than $\pm 20\%$, the data are identified as flawed by "BMB," for bad material balance.

In plotting data, it is normal and too easy to summarily discard any point that falls disturbingly beyond the range that defines any significant correlation. This creates "experimental artifacts," in which data are defined as valid to the extent they support the conclusions drawn from them. In this report, before observing any correlations, identifying a data point as "flawed," on the bases of Table 4, attempts to introduce a less subjective factor in assessing the validity of at least the points that can be so identified. It does not, on the other hand, assure that nonflawed points are, in fact, valid if they fail to fit correlations. These flawed data sets are identified on all following plots as "suspect" points.

Reactivity and potential scaleup data are summarized in Table 5, also divided into three sections. The reactivities are those defined above as k_c , for continuous, completely mixed reactors. An immediate and disappointing observation from Table 5 is that reactivities are, generally, at least an order of magnitude lower than those indicated by TGA tests. As discussed at the end of the preceding section, however, it is apparent that the batch and continuous reactivities, k or k_0 and k_c , are simply not the same property, although clearly related. If one finds a need to design a hypothetical gasification plant on the basis of these data, the key process variable, also from Table 5, is the reactor capacity, $(\text{lb/hr})/\text{ft}^3$, for the same degree of fixed carbon conversion. Finally, if one assumes that 95% conversion can be achieved by simply increasing residence time at the same rate of conversion, the "95% capacity" factor in Table 5 would define reactor size.

6.0 ANALYSIS AND DISCUSSION

6.1 Correlation of Reactivities

For the well-behaved runs summarized in Table 3-B, effective reactivities are correlated with temperature in Figure 6, with the pressures and steam/carbon ratios indicated for each point. Temperature is clearly the dominant variable, to which reactivity, k_c , is most sensitive, and shows a good correlation with the empirical function, mathematically an accelerated parabola, which closely resembles the form of plots relating TGA reactivities, k , to temperature. The constants in this equation were selected to give a visual good fit, and its mathematical form has no known theoretical significance. The single, previously defined "suspect" data point does, in fact, fall the farthest from the correlation. Variation with pressure or steam/carbon ratio, in terms of being above or below the correlation curve, is not consistent, indicating that experimental scatter is at least as great as the sensitivity of the reactivity to these variables.

Figure 7 is a plot of corresponding data from Table 3-A, for uncatalyzed coal in a limestone bed, upon which is superimposed the empirical correlation for K-catalyzed coal from Figure 6. In Figure 7, the single point for 600°C falls above the line for a more reactive, catalyzed reaction and

TABLE 5

Actual Catalyst Levels and Potassium Balance
 Reactivity $K = (dC/dt)C$, $C = \text{Wt. FC in Reactor Bed}$,
 $dC/dt = \text{Rate of FC Conversion to Gas}$

A. Limestone Bed With Raw Coal (K and Fe from coal ash only)							
Run No. M-	216	217	218	220			
	700	600	700	700			
Temperature, °C	2.4	2.4	6.1	2.4			
Pressure, atm							
Reactivity, 1/hr	0.085	0.103	0.203	0.239			
Wt. KOH/Wt. FC	0.005	0.002	0.003	0.003			
FC Conversion	17.9	35.0	55.2	55.1			
% FC in Bed	24.5	44.3	35.4	30.1			
Capacity ¹	0.9	1.7	2.8	2.7			
95% Capacity	0.2	0.6	1.6	1.6			
B. Limestone Bed with K-Impregnated Coal							
Run No. M-	221	222	223	224	225	226	227
	700	600	700	700	650	650	600
Temperature, °C	2.4	2.4	2.4	6.1	2.4	2.4	2.4
Pressure, atm							
Reactivity, 1/hr	0.491	0.053	0.358	0.420	0.210	0.137	0.082
Wt. KOH/Wt. FC	0.165	0.119	0.254	0.319	0.241	0.189	0.153
FC Conversion	75.5	21.4	68.2	69.4	54.8	45.7	29.4
% FC in Bed	19.4	50.8	24.1	18.5	29.3	37.4	40.2
Capacity ¹	3.7	1.0	3.3	3.0	2.3	2.0	1.3
95% Capacity ²	2.9	0.2	2.4	2.2	1.4	0.9	0.4
C. Taconite Bed with K-Impregnated Coal							
Run No. M-	228	229	230	231	233	234	
	600	700	600	700	650	650	
Temperature, °C	2.4	2.4	2.4	2.4	2.4	2.4	
Pressure, atm							
Reactivity, 1/hr	0.408	0.692	0.25	0.357	0.242	0.187	
Wt. KOH/Wt. FC	0.181	0.388	0.183	0.218	0.179	0.169	
FC Conversion	62.9	80.8	57.1	71.6	58.6	50.1	
% FC in Bed	19.4	14.7	28.7	25.2	30.5	33.7	
Capacity ¹	3.0	3.9	2.7	3.4	2.8	2.4	
95% Capacity ²	2.0	3.3	1.6	2.6	1.7	1.3	

¹ Capacity = (lb/hr) cu. ft.

² Projected capacity if residence time were increased to achieve 95% FC conversion at same reaction rate.

Figure 6. Effective reactivity of potassium-impregnated Wyodak Coal in a limestone bed, continuous process data.

Figure 7. Effective reactivity of raw Wyodak coal in a limestone bed, continuous process data.

cannot be explained in light of accepted theory or past relevant data, even though the data set was not identified as "flawed" in Table 4. Taking the middle, nonsuspect point at 700°C as a valid average, the potassium impregnation apparently doubles reactivity, k_c . This is significantly less than the increases in k , indicated in Table 1 for TGA data, but still of substantial practical value if it could double the throughput per capital investment for a real-world gasifier.

Figure 8 is a similar comparison of the taconite bed data from Table 3-C with the empirical correlation from Figure 6. It thus compares the effects of taconite and limestone beds on K-impregnated coal. Although the experimental scatter is wider than for the limestone bed case, it is surprising that five of the six points fall well above the limestone correlation. Based on all known background experience and theory, there is no reason to believe that a valid $k_c(T)$ function would have a dip in it around some intermediate temperature. Therefore, either the 600°C or the 650°C points can be disregarded. It is of interest that the latter were the last two data sets, taken at the end of the second, week-long operating period, which suggests the possibility of some unidentified, systematic operator error, even though the data cannot be identified as "flawed."

What is very encouraging about the data of Figure 8 is that taconite, while of little catalytic value alone, appears at least as desirable as limestone as a bed material for K-catalyzed gasification. There is no explanation why it should actually be better than limestone, in terms of catalytic activity, although that might be inferred from Figure 8. No bed attrition measurements were done in these tests, although some might be inferred from the relative calcium and iron contents of the bed and cyclone

Figure 8. Effective reactivity of potassium-impregnated Wyodak coal in a taconite bed, continuous process data.

ash analyses. Since taconite is substantially harder than limestone, it will probably offer the economic advantage of lower bed makeup costs than for limestone, depending upon source proximity.

As a major but unexpected source of uncertainty in effective reactivities, Figure 9 plots the variation in actual potassium to fixed carbon (K^+/FC) from bed overflow analyses for each of the runs, compared with analyses of the blended feed. The run sequence of the three lines is that of Figures 3-A, B, and C, where the corresponding run parameters can be seen. The original target for feed preparation was the "saturation" line, which is the K/FC weight ratio corresponding to a K/FC molar ratio of 0.12, beyond which, it is believed, further addition of the catalyst results in no further increase in reactivity. This is based on TGA data for an Illinois No. 6 bituminous coal (higher rank) and for wood ("rank" = 0), suggesting that all possible active sites ($-COO^-$, $-CO^-$, and $-C^-$) are saturated with K^+ ions. The fact that the same number results for both cases may be a coincidence; although in the absence of a comparably filled-in k vs. K^+/FC profile of TGA data for Wyodak coal, a 0.12 molar saturation level was assumed here. In spite of care in blending the coal, bed material, and KOH solution, Figure 9 suggests that much of the KOH failed to ion exchange with the coal structure, resulting in loss of catalytic effectiveness. The very low ratio for the single analysis of blended feed for the taconite runs, shown in Figure 9, suggests that segregation even took place during drying, handling, and filling the pressurized feed hopper.

Figure 9. Actual K/FC in reactor bed.

Returning to Figure 8, it is of interest that the extremely high reactivity point at 700°C is for the second run in the taconite series, which was the only one for which the K/FC ratio was at the saturation level and over twice that for any other run. This alone could account for the single high reactivity point. It is also of interest that, through most of the taconite series, the K/FC level was actually below most of the runs in the limestone series, which makes the catalytic performance of the taconite still more impressive. The low and variable K/FC levels in the bed overflow suggest that significant amounts of the KOH are in the form of free dust and are carried out of the bed prematurely.

Material balances on potassium, as well as on calcium, sodium, and iron, showed very poor closure, which is typical of ash components (due to the complexity of oxidation-reduction reactions that occur in the range of conditions in the reaction zone. In XRFA (x-ray fluorescence analyses) of dominant ash components, the nonnormalized data for both the bed overflow and cyclone samples show closures ranging from 55% to 105%, with an average in the mid-80s, with the higher numbers, >100%, occurring mostly in the taconite runs. Standard procedure in these analyses is to normalize raw data, so that percentages of oxides of elements of interest (Al, Si, Fe, Ca, Mg, Na, K, P, Ti, and S) add up to 100%.

Notwithstanding the uncertainty in potassium analyses, an attempt to track the potassium through the process and close a material balance led to an unexplained but clearly significant observation, summarized in Table 6. Analyses of the content of cyclone ash and bed overflow samples, in Tables 3-A, B, and C, and original XRFA data on each, as shown in the examples of Appendix B, all indicate no significant difference in the two streams' composition. Table 6 indicates quite consistent weight distributions of potassium between the two products, the cyclone cut being of finer particle size and carried over with the product gas. As an attempted material balance for potassium, the sum of these product amounts is expressed as a percentage

TABLE 6
Potassium Balances

Bed Material	Limestone	Limestone	Taconite
Catalyst	None ¹	KOH	KOH
Number of Data Sets	3 ²	7	6
% of Ash K ₂ O in Bed ³	88.1	86.6	89.3
% of Input K ₂ O Accounted for ⁴	69.3	34.2	119.8
% Variation in Above Averages, ±	6	8	13

¹ Only potassium present is small amount (See Figure 9) found in coal's ash, initially combined in unknown mineral species.

² One of "suspect" data points (Run M-217) was extremely inconsistent and excluded from average. It is the only data point not included in Table 6.

³ Based on XRFA analyses to determine the weights of K₂O in bed overflow and in cyclone ash, with total = 100%

⁴ Based on input weight of K₂O in feed coal-bed-catalyst ash component, per Table 2, by XRFA.

of the total input potassium, also expressed/assumed as K_2O , as indicated by XRFA analyses. The poor closure is generally attributed to the potassium, as the coal is consumed, reacting with the remaining limestone or taconite, forming mineral species far more complex than the initial KOH. While the extreme variation, from a theoretical 100%, of percentages of presumed K_2O in the feed cannot be explained within the scope of this project, they are strikingly different and extremely consistent within each bed-catalyst category, as indicated by the bottom row of Table 6. Thus the variation in potassium balance closure suggests that potassium, in a high-temperature reducing environment, enters into complex and quite different inorganic reactions with the limestone and taconite.

As to coal feed preparation, all the potassium was impregnated onto the coal from solution before the coal was mixed with limestone or taconite, so that variation in potassium actually present in the reactor bed, as tracked in Figure 9, was earlier assumed to be a result of errors or randomness in impregnation procedure. It has also been assumed that the standard XRFA is consistent and accurate in identifying the key inorganic elements, expressed as equivalent weights of oxides. In the light of Table 6, there now appears some doubt as to whether XRFA identifies all of the potassium present. This, if possible, in turn suggests the possibility that during the taconite runs some significant amount of potassium, undetected by XRFA, may have, in fact, been present, contributing to the high reactivity. The wide but consistent difference in K-balance closures between limestone and potassium could also imply that much of the potassium in the limestone bed may be tied up in some XRFA-invisible form, such as amorphous compounds. Another possibility is that some elemental potassium, produced in the reducing atmosphere, may simply vaporize, to be condensed with the water, which was not analyzed in these tests.

Early in the past year of this project, tentative plans were made to consider the use of a potassium-impregnated taconite bed material on the 40-lb/hr PDU scale, based on preliminary TGA tests. This would have required an auxiliary, high-temperature process to prepare the sintered potassium-taconite catalyst material. These plans were canceled, however, as the project scope became limited by time and funds available. It was also decided that, in the interest of process economics, bed materials would be limited to cheap, disposable materials, such as the limestone and (site-specific) taconite. It would now appear that long-term development should not rule out synthetic, recoverable bed-catalyst materials. While near-complete recovery of potassium is clearly essential to economic viability (2), studies on external bed regeneration or recovery must be justified by estimates of their process costs as a trade-off against replacement costs. The only leaching studies at the EERC to date (2) have dealt with the extraction of potassium from mixtures of gasifier coal ash and wood ash. The possibility of stable potassium-iron compounds, intentional or inherent, may complicate the recovery problem. It is worth noting that a successful pressurized, fluidized-bed gasification program, by the Institute of Gas Technology (10) has used durable ceramic spheres as a bed material, essentially eliminating bed replacement costs. This suggests that such spheres could be made of some methane-catalyzing, taconite-derived substrate that might hold saturation levels of potassium in some catalytically useful form.

The above discussion and Table 6 clearly raise more questions than they answer. However, the following conclusions and recommendations can be supported:

1. The chemical form and probably the mobility of potassium in the reactor bed is dependent upon its interactions with the bed material, which, though still unknown, are very different for limestone, taconite, and coal ash.
2. Standard analytic means of tracking the potassium through this process are now suspect, requiring review or new procedures development.
3. EERC has extensive experience in sophisticated studies of mineral transformations during combustion. Any future work in catalytic gasification should include application of some of these more rigorous methods of tracking potassium or other catalysts through the process.
4. As longer-term research, more sophisticated, synthetic bed materials, such as potassium-impregnated, iron-ceramic spheres, should be investigated, at least by bench-scale tests.

Returning to the above discussion of the possibility of labile or free floating potassium, probably as K_2O or KOH , in the reactor bed, there is a more sinister possibility of it causing agglomeration and some loss of fluidization, since the melting point of anhydrous KOH is only $360^\circ C$. While there was no firm evidence of bed plugging during the runs reported here, even minor, intermittent agglomeration could result in incomplete fluidization and channeling, which in turn would introduce random variation in the residence time and thus the reaction rates. In a slightly earlier, parallel project (3), similar tests were done using wood in place of coal, catalyzed by massive admixture of recycled ash. Even in the best of cases, wood is difficult to fluidize. With the ash addition, the bed frequently became plugged, exhibiting massive clinkers when shut down. It should be kept in mind, at this point, that if a fluidized-bed reactor has any possible reason for plugging or channeling, the probability of it happening increases sharply with decreasing bed diameter.

These wood gasification tests made a major contribution to this project, leading to the decision to make these final coal tests with impregnated (homogeneous) catalyst impregnation, rather than simply cofeeding dry (heterogeneous) KOH catalyst. This is also consistent with earlier experience in the EERC 40-lb/hr PDU (4), in which sodium-bearing trona and nahcolite catalysts were cofed with Wyodak coal, resulting in bed plugging by quite large agglomerates.

One of the "loose ends" of this project is the knowledge that, according to TGA data, sodium is as good a catalyst as potassium and would be far cheaper. However, no continuous tests have been done with homogeneous sodium catalyst, impregnated from solution, as was done in these tests with potassium, to determine whether the agglomeration problem can thus be avoided. Similarly, the EERC has done no continuous PDU tests with heterogeneous (cofed) potassium-bearing catalysts, for comparison with the earlier trona and nahcolite tests. Qualitative observation of material remaining after TGA

tests indicates that the tendency of bituminous coals to agglomerate was apparently significantly reduced by adhesion of K_2CO_3 , presumably reduced to K_2O . The definitive work by Exxon (8) at least reports no agglomeration problem using K_2CO_3 , while personnel at IGT (10), gasifying wood and coal in a pressurized fluidized bed similar in concept to the EERC PDU, report verbally that some agglomeration was observed using potassium salts, consistent with EERC's experience with wood (4).

An interesting correlation of reactivity data is shown in Figure 10. Here the effective reactivity, k_c , defined as lb/hr of fixed carbon consumed per lb of fixed carbon in the bed, is plotted against the percentage of fixed carbon in the bed. A significant uncertainty in computing k_c is estimating the FC weight in the bed, which is a function of particle density and void fraction, neither of which can be observed directly under reaction conditions. In Figure 10, for design purposes, k_c , determined from a plot such as Figures 6, 7, or 8, is actually the independent variable, while the %FC will reach some equilibrium defined by the empirical correlation shown in Figure 10. It is of interest that, at this point, temperature, pressure, steam/carbon ratio, and catalyst selection are essentially out of the way as design variables. For this reason, no legend is given to identify the three kinds of symbols, corresponding to the data sets of Tables 3-A, B, and C.

Figure 10. Effective reactivity vs. % fixed carbon in reactor bed, composite for all runs.

Finally, instead of the reactivity, the more directly applicable design parameter, specific capacity, SC, defined as lb/hr of FC consumed per reactor volume, is also plotted against %FC in Figure 11. The reactivity correlation from Figure 10 is added for comparison. This simple, straight line function, $SC = f(\%FC)$ says, in effect, that when changing any operating conditions, feed, or catalyst to enhance reactivity or specific capacity, the equilibrium %FC in the fuel bed will reach an equilibrium given by the line of Figure 11. It must be emphasized that Specific Capacity is a feed-catalyst-bed-condition material property. Changing the feed rate or the bed volume, limited by the overflow level, will require computing a new SC, which is simply the rate of FC consumption by a new reactor volume. This was done in Table 5 for an assumption of 95% complete FC consumption, resulting in far lower SC values. Also of interest in Figure 11 is that SC and k_c are obviously related, but not in linear proportion.

6.2 Supporting TGA Data

The theoretical discussion of Section 4 is based on an assumption that the fixed carbon fraction of a coal has a certain reactivity that is constant even as it is depleted to very low levels. This presumes that the reactivity of even a low, but constant, level of fixed carbon in a fluidized-bed gasifier has the same TGA-determined reactivity that it did when fed, even though the rate of reaction, $-dC/dt$, is greatly reduced. This raises a question of whether a coal's reactivity actually reflects a composite of various different chemical structures, such as the different macerals, that may individually

Figure 11. Fixed carbon conversion (specific capacity) vs. fixed carbon content of reactor bed.

have different reactivities. To support the assumption that reactivity is in fact a constant and uniform property, retained samples of the blended feed for two of the runs reported here were submitted for TGA analyses, along with samples of the bed overflow material. These results are presented in Table 7. Comparing the TGA reactivities of feed with overflow product, for both feed mixtures, confirms that reactivity is, in fact, constant with time and with fixed carbon consumption.

The two runs checked by the TGA analyses of Table 7, though at different temperatures, were selected because both are non-"suspect" data points and are extremely close to the same empirical correlation line of Figures 6 and 8. (These are also the data sets presented in their entirety as Appendix B.) Also of interest is the reduction of reaction order in these samples. The taconite samples (feed and product) were noticeably less than first-order, while the more heavily catalyzed limestone samples appeared to be actually closer to zero order. In a zero-order reaction, the rate, $-dC/dt$, is essentially constant and independent of the amount of fixed carbon remaining. That is, the reaction will be faster at low levels of remaining fixed carbon. This is certainly desirable to reduce reactor size for a required throughput.

Table 7
Comparison of TGA Reactivities on Blended Feed
and Residual Bed Material

Run Number	M-224	M-233
Bed Material	Limestone	Taconite
Catalyst and Coal	KOH-Impregnated Wyodak	KOH-Impregnated Wyodak
Temperature	700°C	650°C
% FC Consumed	69.43	58.63
% FC in Reactor Bed	24.1	30.46
CPU Reactivity, k_c , 1/hr	0.42	0.24
TGA Reactivity, ¹ k , 1/hr		
Feed Material	3.97	3.31
Bed Overflow	3.79	3.34
Ratio, k/k_c		
Feed Material	9.45	13.79
Bed Overflow	9.02	13.91
TGA Reactivity, ² k , 1/hr		
Reaction Order	0	1-
Feed Material	2.93	2.45
Bed Overflow	2.35	2.89
Ratio, k/k_c		
Feed Material	6.98	10.20
Bed Overflow	5.52	12.04

¹ Assumed first-order reaction, per standard simplifying assumption.

See Appendix A for definition and significance of reaction order.

² Calculated reaction order, also per normal TGA procedure.

Since no consistent rule to predict reaction order has been identified, the normal first-order assumption, which is the basis of all assumptions discussed above, provides a conservative estimate of reaction rates. To the extent that relative reactivities are used to compare or predict gasifier behavior, real-world reaction rates are more likely to be greater, than less, than predicted.

Figure 12 shows a correlation between the specific capacities, $(\text{lbFC/hr})/\text{ft}^3$, and CPU-determined reactivities, $1/\text{hr}$, for all of the K-impregnated coal runs. Superimposed on these data are two points correlating the TGA data on residual, in $1/\text{hr}$, correlated with two corresponding values of k_c , in $1/\text{hr}$. These two points do not have the same units as shown on the vertical axis of Figure 12, but are numerically consistent with the other points and, insofar as two points can define an empirical function, appear to vary in the same proportion.

6.3 Gas Yields and Compositions

Plots of the product gas composition and yield data of Figures 3-A, B, and C were generally disappointing. Variation with pressure, steam-carbon ratio, and bed or catalyst selection was less than the experimental scatter, which is attributed mainly to the uncertainty in gas flow measurements discussed earlier. When all data are averaged for each temperature point, the results show the variation with temperature shown in Figure 13, which is consistent with theory and expectations. Only with temperature was the variation greater enough (than the experimental scatter) to enable correlations with any statistical validity.

Figure 12. Comparison of reaction rate measurements.

Figure 13. Average gas yield summary.

Plots to show whether the use of a taconite bed increased methane content of the product gas or methane yield per MAF or FC consumed showed no correlation. It is probable that longer tests at the same sets of conditions, such as 24 to 36 hours, with multiple material balance periods with multiple gas and solid samples taken during each period, would have yielded statistically valid data, such as the temperature correlations of Figure 13. This approach, though expensive, is under consideration for future tests in a parallel project using Illinois No. 6 bituminous coal.

It must be emphasized that for this report single data points were rejected as "flawed" or "suspect" only for reasons other than simply not falling close to a desired correlation curve. For a data base of too few points for valid statistical correlation, at any one set of conditions, arbitrary rejection of points would reduce correlations to creative experimental artifacts. (This is very analogous to an attorney's freedom to reject jurors "for cause" who appear unlikely to render a desired verdict.) The only exception in this case was Run M-217, with limestone bed and no KOH, at 600°C, which showed a methane yield simply far too high to be believable. This run also shows an unbelievably high yield, considering the lack of KOH catalyst, in Figure 7 and is excluded from the 600°C averages of Figure 13.

7.0 INTEGRATED BENCH-SCALE GASIFIER SHAKEDOWN DATA AND POTENTIAL

A newly developed research tool at EERC is the integrated bench-scale gasifier (IBG), in which a sample of 200 to 300 g of coal is injected into a preheated fluidized bed. After a selected reaction time, the entire bed is

dumped and quenched, while all gas, condensable, and solid products are saved for analysis. This differs from the TGA in that the particle heatup rate in the IBG is essentially instantaneous, as when coal is fed into a fluidized-bed gasifier, so that devolatilization and the steam-char reactions start concurrently. This unit was initially conceived to enable production of samples of char and condensable liquid products big enough for analysis, far more cheaply than possible using the CPU. Unlike the TGA apparatus, the pressure rating of the IBG is 150 psig. The unit is also provided with a hot sampling probe immediately over the bed and optical windows to enable on-line studies of the hot gases by mass spectroscopy, atomic absorption/emission spectroscopy and FTIR (Fourier transform infrared) analysis.

During the brief test period, using a constant stream of preheated steam and nitrogen for fluidization, the carbon monoxide level in the product gas is measured continuously. Since the amount of CO, or any other product gas, is a fair measure of the rate of reaction, this easily observed variable becomes a reaction rate measurement, directly equivalent to the rate of weight change in TGA tests. For a recently completed shakedown test, a CO(t) plot is presented in Figure 14, along with analyses of it performed by a data reduction program. Also shown on the plot are the periods of opening and closing the feed and discharge valves, arranged as shown in the system sketch of Figure 15, and the point at which a gas sample is taken for analysis. Feed gas streams may include any mixture of gas, simulating different process concepts, and multiple product gas samples may be taken.

Figure 14. Typical IBG data sample.

Figure 15. The EERC integrated bench-scale gasifier (IBG) schematic.

The most significant data treatment is the numerical integration shown in Figure 14, which defines a function proportional to the momentary weight of the decreasing amount of fixed carbon in the charge. With initial and final sample weights, and intermediate weights prorated according to the curve, reactivities can be calculated for direct confirmation of TGA data.

Another mathematical treatment of the data is the double exponential empirical function shown on Figure 14, in which reactivity, k , a much faster warmup rate constant, k_r , related to the heat-transfer behavior in the bed, and an overall scale factor, S , are juggled by trial and error to achieve a visual best fit to the portion of the curve representing the rate of the gasification reaction, as shown. Further sophistication could add automatic,

iterative calculations to generate a least squares best fit for these functions. Since taking the derivative or integral of an exponential changes only the scale factor, the k in the empirical function is expected to show a good correlation with the corresponding reactivity computed from the weights and the empirical integral function. The initial hump, rising beyond the two computed functions, is believed to represent an additional CO release during devolatilization or pyrolysis. The empirical function can also be juggled to show a fair correlation with the devolatilization hump, which is of relatively little interest, but not with both sections of the curve. Gas samples taken around the devolatilization peak may indicate differences between pyrolysis gases and gasification products.

As of this writing, the IBG system is scheduled for near-future use as the major process projection tool in two related projects, both dealing with production of hydrogen and methane from bituminous coal for fuel cell applications. Another potential application for this unit is in the development of more advanced bed-catalyst combinations, such as a potassium-iron-ceramic bed material suggested in Section 6.1 above.

8.0 COMPARISON WITH 40-LB/HR PILOT-SCALE DATA

A preliminary report of the last series of runs was included in the previous semiannual project report (2). The objectives of this run series were to confirm operability and to generate baseline data for Wyodak coal with limestone alone, in preparation for later runs with impregnated KOH catalyst and limestone or taconite beds. Following the massive reconfiguration of the combined gasifier system during 1990, for hydrogen production, mild gasification, and pressurized fluid-bed combustion, this run series was intended to establish continuity with a series of Wyodak-limestone runs (4) completed in 1988. Unfortunately, the PDU was not in as operable a condition as expected, requiring four shakedown runs to identify problems and make somewhat costly modifications as needed, mainly with respect to instrumentation, hot-gas cleanup, gas quenching/scrubbing, and increased pressure ratings of associated piping. By the completion of the last run series of 1991, reported here, the project budget was partially depleted ahead of schedule, and a decision was made to complete testing in the much smaller-scale CPU system. A major goal of the system modifications was achieved, in that the PDU system was left in as-designed, operable condition, available for future gasification tests. Due to decisions beyond the scope of this project, however, the gasifier itself was subsequently dismantled, to make room for a planned transport reactor or fast circulating bed gasifier.

For comparison with the above CPU data, the essential data from these three PDU runs are summarized in Table 8-A and 8-B. The nominal 40-lb/hr PDU is a complete process simulation in that the required heat is supplied internally, by combustion of part of the coal feed. As expected, gas compositions are somewhat higher in CO₂ and correspondingly lower in other components, but represent a credible gas composition to assume for a commercial-scale design.

As configured for these runs, the gasifier had no bed overflow, so that bed level was determined by the feed and reaction rates and was observed as a temperature profile, indicated by in-bed thermocouples. The unit was provided with a vertical, top-entry bed sampling probe that became plugged and proved

unworkable, so that bed samples were available only at the end of the third run, when the vessel was opened for cleaning, yielding the end-of-run bed analysis of Tables 8-A and 8-B. An element of uncertainty is created by how instantly the entire bed is effectively quenched at shutdown. The effective intervals between sequentially turning off coal feed, oxygen, and steam and turning on a quench stream of nitrogen are limited by computer-operator response times and the thermal inertia of the system. Consequently, the carbon content of the single bed sample is probably somewhat lower than was typical during operation.

Throughout this report, reactivities and specific capacities have been computed as $(dC/dt)/C$, defining C as fixed carbon (FC), as determined by a standard proximate analysis, to be consistent with definitions established by TGA tests. In the earlier phase of this project, reactivities were based on total carbon, as determined by a standard ultimate analysis, as was also done by Exxon (8) in what is considered the definitive early work on potassium-catalyzed coal gasification. For this report, however, the FC-based definition was used because it is the reaction of steam with char, as measured by TGA, that determines overall reaction rates. Much of the total carbon is

Table 8-A
Data Summary for 40-lb/hr PDU Tests

Objectives	1. Confirm operability	2. Baseline data
Feed	Wyodak Subbituminous	
Fluidized Bed	Limestone: 35 lb	
Catalyst	None (Intrinsic)	
Run Duration	44 hours	
Each Material Balance	2 hours	
Btu/lb		
As received	8,945	
Dry	11,060	
	<u>Feed</u>	<u>Bed¹</u>
Feed Proximate Analysis, wt%		
Moisture	19.10	
Volatiles	37.30	
Fixed Carbon (FC)	38.50	
Ash	5.10	
Ultimate Analysis, wt%		
Hydrogen	6.1	0.60
Carbon	52.88	5.40
Nitrogen	0.65	0.10
Sulfur	0.51	0.20
Oxygen	34.73	0.00
Ash	5.11	93.70

¹ At end of Run -3, indicating 90%+ carbon depletion.

Table 8-B
Data Summary for 40-lb/hr PDU Tests

Run No. H ₂ -91-5	-1	-2	-3
Temperature, °C	754	702	652
°F	1390	1296	1205
Pressure, atm	1.1	1.2	1.2
Coal Feed, lb/hr	25.5	17.0	17.0
Oxygen, lb/hr	16.0	12.7	10.2
Steam, lb/hr	27.2	26.9	27.7
Steam/FC, Mol/Mol	1.8	2.7	2.8
Product Gas,* lb/hr	29.1	31.9	29.3
scfh	498	535	495
Analysis, Mol% H ₂	42.0	42.5	44.7
(Dry, N ₂ -free), CO	16.5	12.0	9.1
CO ₂	37.4	41.6	43.0
CH ₄	3.0	2.8	2.6
H ₂ S	0.1	0.1	0.1
C*	1.0	0.9	0.5
Cyclone Fines, lb/hr	2.63	3.80	4.10
Hydrogen %	1.08	1.68	1.90
Carbon %	54.20	69.31	70.00
Nitrogen %	0.70	0.98	0.86
Sulfur %	0.96	0.33	0.42
Oxygen %	1.08	7.10	7.04
Ash %	41.96	20.60	19.78
Gas/MAF Fed, scf/lb	25.79	41.33	38.43
Gas/FC Fed, scf/lb	50.77	81.38	75.67
Gas/C Fed, scf/lb	36.96	59.25	55.09
Gas/C Converted, scf/lb	41.33	83.80	80.93
H ₂ /C Converted, scf/lb	8.12	5.48	5.75
CH ₄ /C Converted, scf/lb	1.26	2.38	2.12
Carbon Converted, scf/lb	89.4	70.7	68.1
Min. ¹ specific capacity			
(lb FC/hr)/ft ³	8.88	4.68	4.51
(lb c/hr)/ft ³	14.19	9.46	9.46

¹ Assuming maximum bed depth of 4 ft (at ID = 6.5")

included in volatile components, which break down to form product gas by other reactions which are substantially faster, as described in Appendix A. In short, the overall gas production rate is determined by that portion of the carbon that reacts relatively slowly with steam.

The bed was not drained between runs. Due to an operational oversight, the residual bed material at shutdown was not weighed. Consequently, no calculation of reactivity based on weight of carbon, fixed or total, in the bed was possible. From a design point of view, specific capacity is more directly useful. As another oversight, no proximate analyses were ordered for the end-of-run bed sample. It can be reconstructed from the ultimate analysis, however. Going back to the CPU product char analyses for all the runs of Tables 3-A and 3-B, it was found that the ratio of FC(prox.)/C(Ult.) is a remarkably constant 0.7, with a random variation of less than 10%. Therefore, the amount of total carbon leaving the PDU in cyclone ash was multiplied by 0.7 and subtracted from the fixed carbon to determine an approximate carbon consumption rate. With the fluidized-bed depth of four feet, observed in the form of a temperature profile, the effective capacities, in (lb FC/hr)/ft³ at the bottom of Tables 8-A and 8-B, were determined. Also reported for comparison is the specific capacity in terms of total carbon per hour per bed volume.

For comparison with CPU results, for the limestone and limestone+KOH cases, effective reactivities are plotted in Figure 16. The lines added to Figure 16 are again an accelerated parabola correlation, similar to that defined in Figure 6, at two different 580°C intercepts. Although the number of points is few and the experimental scatter great, it appears that the PDU specific capacity (SC) for Wyodak coal with limestone, at about 70% carbon conversion, is roughly 2.5 times that derived from the CPU data, at 55% carbon conversion. If the CPU SC figures were increased by 70/55, reflecting a longer residence time for more complete reaction, this disparity would be reduced, but far from eliminated. If the volumetric reaction rate is assumed proportional to pressure, and the PDU SC increased by 2.4/1.2, reflecting the operating pressures in atmospheres from Table 3-A and Table 8, this disparity will be increased further.

In conclusion, the PDU tests were successful in demonstrating operability of the recently modified system and indicate performance generally comparable to that reported in the earlier phase of this project. Unfortunately, broader EERC priorities required dismantling the reactor vessel to make room for the expected transport reactor, thus precluding the possibility of proposing any near-term follow-on efforts in this area. Because the PDU is a more complete process simulation, its specific capacity data inspire greater confidence than the CPU results, in spite of operational difficulties in the brief run series reported here. The use of CPU data is thus recommended as a lower-cost basis for preliminary process design because it is clearly conservative with respect to reactor capacities. Overall conclusions are summarized in Section 1.

9.0 PROJECT EVALUATION AND RECOMMENDED FUTURE EFFORTS

9.1 Evaluation

In regard to the project goals, restated in Section 3.1, The data reported here and in previous reports establish that potassium-impregnated coal shows a substantially higher reactivity in a fluidized bed of limestone or taconite, while limestone alone is established at least as a fair catalyst, with the advantage of being disposable. "Loose ends" worthy of interest include the unexplained, but apparently beneficial, interaction between KOH and taconite, plus the possibility that sodium may be a cheaper alternative to

Figure 16. Specific capacity, PDU data.

potassium, depending on how it is applied to the coal during gasification, that is, homogeneously (impregnated) or heterogeneously. In general, identification of chemically desirable or optimal catalysts has not resolved the mechanical distribution or bed management aspects of applying them to the coal during reaction.

The project as a whole has proven to be a bit overscoped, with too many digressions and ramifications for the budget in the final two years of effort. The objective of extending catalyst optimization to the production of liquid and char products never moved much beyond the planning stage, since they were not directly related to hydrogen production, nor to the more pressing need to develop continuous catalytic gasification data. The design and construction of the IBG were originally intended for this application, however.

Some theoretical effort was expended on kinetic modeling and yield prediction, but never proceeded beyond a simple equilibrium model. This study, requiring no laboratory efforts, is still "on hold" and will be pursued under subsequent Cooperative Agreement efforts. This will include obtaining the best nonproprietary computer modeling software and adding provisions for including the effects of catalysis.

The possibility of in-bed sulfur capture was one of the motivations in selection of taconite as a bed material. However, because of the low sulfur content of the Wyodak coal, selected under EERC's mission to concentrate on low-rank coals, sulfur levels in ash and gas were too low to yield significant conclusions, within the range of experimental scatter. At present, the EERC has firm commitments, starting in the imminent projects for the new fiscal

year, to continue efforts to control the effects of sulfur and other undesirable trace elements, using both the IBG and CPU hardware.

9.2 Possible Follow-On Efforts

Starting on the smallest physical and economic scales, several of the pending questions or "loose ends" described above appear worthy of further effort. Primarily, the question of how potassium, and possibly sodium, should best be impregnated upon the feed coal and what kinds of complexes they may form on limestone or taconite bed material during reaction can be explored on a small scale. The IBG unit may prove quite valuable as a screening tool for this type of study.

It is expected, however, that further CPU runs would be needed, primarily to achieve long-term equilibrium with regard to mineral transformation reactions. This would best be accomplished by relatively long CPU runs, perhaps of a whole week, at each of a very few sets of conditions, with multiple replication of material balances and sample analyses. This would also provide statistical confirmation of the relative rating of the three bed + catalyst systems studied here. Such runs should be at the highest pressures possible to explore the probable enhancement of methane production, as a desired component in gas feeds to advanced fuel cells. It is of interest here that the EERC is presently committed to remodeling the CPU system, over the next two years, to operate at substantially higher pressures.

As originally stated, all the original objectives of this project had to do solely with the chemistry of catalytic gasification for hydrogen and methane production. As a valid generality, most of the loose ends discussed herein deal with mechanical aspects of continuous processes, such as bed distribution and agglomeration, all of which are exacerbated in minimum-scale continuous testing. There is thus a need for larger scale, at least 100-lb/hr, process demonstration tests to identify and solve these mechanical design problems. The PDU operations described here, and in earlier project reports (4), were too brief and attempted to cover too broad an experimental matrix to truly qualify as a process demonstration.

EERC has on hand all of the components of a 30,000 scfh, slagging, fixed-bed gasifier system that achieved successful operation in 1982 (11, 12). The vessel, which is certified for about 550 psig and equipped with a generous profusion of large nozzles, was last used with a 29-inch inside diameter, with 6 inches of refractory lining. This vessel could easily be reassembled and modified for an impressive variety of different fluidized-bed designs. Based on the last inside diameter, such a PDU would offer roughly twenty times the capacity of the PDU runs reported above, or 500 lb/hr of Wyodak coal feed, at 750°C, producing nearly 10,000 scfh of gas, at near atmospheric pressure, or much higher rates at higher pressures. In its 1979-1983 project period (11, 12), it was operated at pressures up to 300 psig. Most of the components are still present and recoverable. The major new component needed would be a screw feed system, in turn fed from lock hoppers, to convert it into a bottom fed, fluidized-bed system. The size of such a unit would provide a very realistic, integrated demonstration project, which could include a next-generation, state-of-the-art hot-gas cleanup system and an advanced molten carbonate fuel cell by Energy Research Corporation, or possibly multiple fuel cells by different manufacturers. It would also allow considerable latitude in the design and redesign of internals to optimize bed behavior. Such a

demonstration system, to be justified, would have to be financed for semicontinuous operation for several years, with its own operating staff and no priorities or agendas overlapping those of other EERC projects.

The reassembly and shakedown operation of such a system can be accomplished at substantially reduced cost by the use of existing hardware, although construction and shakedown operation costs will still be on the order of several million. In view of the reconfirmed certainty, described above and in various parallel works (7-9), that enhanced reaction rates by potassium plus limestone and probably taconite is desirable, a demonstration project would be the logical next step to commercialization.

Finally, in view of the cost of the recommended expanded-scale efforts, a careful review of all "available" fluid-bed gasification technology should consider that current state of the art is now defined to point where a demonstration project is justified. In short, the question is whether further pilot-scale efforts to merely determine that fluidized-bed gasification works are justified, unless some truly novel mechanical design needs a proof-of-concept demonstration. PDU-scale, or smaller, studies of process chemistry are clouded by mechanical design issues, as indicated in this report, that may not be clearly resolved on this scale, may not be relevant in a commercial-scale system, or may require quite different design solutions on a larger scale.

The recommended demonstration plant would be a complete gasifier system, based on the most convincing available reactor designs, integrated with a utility plant, which could provide coal preparation, process steam, cooling water, ash disposal, and other off-site and auxiliary functions at the utility's internal, variable cost, thus greatly reducing the capital and operating costs required for a completely autonomous pilot project. The product gas, following cleanup steps, could be consumed by on-site, or near-site, fuel cells, as an integrated demonstration. Or, as a minimal effort, the hot, uncleaned product gas could be fed to the utility's boilers at a cost per Btu equal to the raw coal, thereby recouping at least part of the subsidized cost of the demonstration project. If the selected demonstration site should have a cyclone-type boiler, the gasifier's product could be used in the reburn mode, introduced downstream of the very hot cyclone burner, to reduce NO_x formation (13, 14). Normally, natural gas is used for this purpose, thus setting a substantially higher value on the gasifier's product.

With such a demonstration plant once in continuous operation, using raw coal in a limestone bed as the simplest and cheapest process option, it would provide a site at which other process options could be tested at relatively little additional cost. For example, substituting taconite for limestone for a few weeks of operation would entail little more than some differential transportation cost. Potassium-impregnation of a week's supply of coal would require some additional feed preparation equipment that would be substantially cheaper than building a separate gasifier PDU.

The scale of such a demonstration project, while limited by the funding level available, should also be influenced by the possibility of its being economically self-sufficient in operating costs. To project such scale-dependent costs, it is essential to determine whether such a major step toward commercialization should be undertaken, rather than to build a bigger PDU. Clearly, the demonstration program will serve a wider range of technical

and political objectives than further exploration of process chemistry by PDU efforts. Economic bases for such a determination can probably be established by one or two man-years of feasibility study, focused on selected utility plant sites.

10.0 REFERENCES

1. Hauserman, W.B. "Production of Hydrogen and By-Products from Coal: Final Executive Summary," (Title subject to minor changes) USDOE Contract No. DE-FC21-86MC10637, 1992, in preparation.
2. Hauserman, W.B. et al. "Production of Hydrogen and By-Products from Coal," Semiannual Technical Progress Report, July 1 - December 31, 1991.
3. Hauserman, W.B.; Timpe, R.C. "Catalytic Gasification of Wood for Hydrogen and Methane Production," final report, Work done for US Dept. of Agriculture and the University of Minnesota, January 16, 1992.
4. Sears, R. et al. "Production of Hydrogen from Low-Rank Coals, Hydrogen-from-Coal Continuous Process Unit Testing," topical report, USDOE Contract No. DE-FC21-86MC10637, August 1989.
5. Timpe, R.C. et al. "Production of Hydrogen from Low-Rank Coals, Char Properties and Reactivities," topical report, USDOE Contract No. DE-FC21-86MC10637, May 1989.
6. Sinor, J.E. "Production of Hydrogen from Low-Rank Coals, Industrial Market Assessment of the Hydrogen Produced from Low-Rank Coals," USDOE Contract No. DE-FC21-86MC10637, July 1988.
7. Stoddard, L.E. et al. (Black and Veatch Inc.) "Production of Hydrogen from Low-Rank Coals," final report for period ending May 1, 1989, USDOE Contract No. DE-FC21-86MC10637, 1989.
8. Kalina, T.; Nahas, N.C. (Exxon Research and Engineering Company) "Exxon Catalytic Coal Gasification Process Predevelopment Program, Final Project Report," USDOE Contract No. E(49-18)-2369, December 1978.
9. Meyers, S.A.; Tanner, A.L.; Moss, T.E. (Fluor-Daniel Inc.) "The Design of Gasifiers to Optimize Fuel Cell Systems, Final Report," Prepared for Energy Research Corporation, October 1991.
10. Evans, R.J. et al. (Institute of Gas Technology) "Development of Biomass Gasification to Produce Substitute Fuels," Project 65058 Final Report, USDOE Contract No. B-C5821-A-Q, March 1987.
11. Hauserman, W.B.; Willson, W.G. "Conclusions on Slagging, Fixed-Bed Gasification of Lignite," 1983 Lignite Symposium, Grand Forks, North Dakota, May 18-19, 1983.
12. Hauserman, W.B.; Willson, W.G. "Mechanical Problems in the Design of a Fixed-Bed, Slagging Gasifier," ASME Energy-Sources Technology and Exhibition, Houston, TX, Jan. 30 - Feb. 2, 1983.

13. Farzan, H. et al. (Babcock & Wilcox, EPRI and IGT) "Pilot Evaluation of Reburning for Cyclone Burner NO_x Control," EPRI/EPA Joint Symposium on Secondary Combustion NO_x Control, San Francisco, CA, March 1989.
14. Yagiela, A.S. et al. (Babcock & Wilcox) "Update on Coal Reburning Technology for Reducing NO_x in Cyclone Boilers," *In Proceedings of the 1991 Joint Symposium on Stationary Combustion NO_x Control*; EPRI GS-7447, Project 2154, Nov. 1991.

13. Signature of Recipient and Date
W. F. Finkelman, July 29, '92

14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10837		2. Program/Project Title Production of Hydrogen and By-Product from Coal (6.1)		3. Reporting Period 4-1-92 through 6-30-92	
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000				5. Program/Project Start Date 4-1-88	
				6. Completion Date 9-30-92	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	Gasification Kinetics:				
a.1	Evaluation of catalysts for gas production (Topical Report)	12-31-91			
a.2	Char surface properties measurement and control (bench-scale and IBG)	12-31-91			
a.3	Evaluation of catalysts for liquid production (IBG scale)	6-30-92			
a.4	Topical report on catalytic effects in char and liquid production	6-30-92			
Task B	Production of Carbon, Liquid, and Gas By-Products:				
b.1	Construction and shakedown of IBG system	9-30-91	1-24-92		
b.2	Vortex venturi cold testing and evaluation	9-30-91	1-24-92		
b.3	Activated carbon lab-scale production and testing (IBG-scale)	12-31-91			
b.4	Subpilot-scale activated carbon production (1-4 lb/hr continuous)	6-30-92			
b.5	Liquid product lab-scale production and testing (IBG-scale)	6-30-92			
Task C	Gas Conditioning and System Integration (evaluation of pilot-scale work conducted under Hot-Gas Cleanup task, relative to hydrogen production application).				
Task D	Pilot-Scale Hydrogen Production:				
d.1	Evaluation of catalyst behavior during extended operation	12-31-91	12-31-91		
d.2	Vortex venturi hot (in-process) testing and evaluation, pending encouraging results of Task b.2.	3-31-92			
d.3	Catalyst evaluation topical report	6-30-92			
Task E	Final Report	8-31-92			

APPENDIX A
THE DEFINITION AND MEASUREMENT OF CHAR REACTIVITY
IN COAL AND WOOD GASIFICATION PROCESSES

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GASIFICATION REACTIVITY DEFINED

The objective of gasification of coal or biomass is to convert the solid feed to the maximum possible amount of organic gases and/or condensible vapors, at the maximum possible rate, consuming the minimum heat from partial combustion of feed to supply the heat of reaction. This transition from solid carbon to a highly variable mixture of gases during gasification is the result of a complex interplay of many different chemical reactions. The overall rate is dominated by the well-known steam-char reactions:

and

There are of course many concurrent reactions that happen, at various rates determined by distribution of intermediates in reacting system, by temperature and pressure, by the presence of catalysts and by the structure of the carbonaceous feed. The most significant of these are described below.

Volatilization and thermolysis (cracking) of hydrocarbons and heteroatom-containing hydrocarbons which can be represented by:

These reactions proceed quite rapidly and may account for H_2 and CH_4 , but are dependent only on temperature, pressure, and the chemical nature of the feed, being influenced only slightly by the gaseous product concentration and

shifting:

methanation:

whose rates are limited by the rate of CO and H_2 produced by the steam-char reaction, and

combustion:

which is essentially instantaneous, compared with the above reactions, and is controlled only by the amount of oxygen available in the reaction system.

finally:

which is a fairly slow reaction producing a significant amount of methane in an H_2 -rich environment, where its rate will be determined by H_2 availability.

Thus the rate of the steam-char reactions is the dominant factor that controls and limits the overall rate of carbon consumption. Reactivity is defined as the property of any char that is defined by its rate of reaction with steam. By definition, char is any carbonaceous material that has been thermally stripped of any volatiles as well as moisture by the above cracking reaction.

Reactivity is that basic property of a coal or wood char that determines whether gasification can proceed rapidly enough at a prescribed set of conditions of temperature and pressure to justify further process research. It provides information regarding the required temperatures and residence time in a gasifier vessel, which in turn serve as basis for design of the vessel of desired throughput capacity and ultimately determine the capital investment in that vessel.

Laboratory-scale measurement of reactivity is done by thermogravimetric Analysis (TGA) in a device shown schematically in Figure A-1. As temperature is increased to the desired gasification temperature with the sample chamber swept by inert argon to remove volatiles, the sample weight decreases as shown in Figure A-2, until the weight loss curve, dW/dt levels out, indicating that all volatiles have been removed. The remaining, thermally stable char which generally includes over 50 wt% carbon, is then reacted with superheated steam. The char carbon is consumed by the steam-char reaction at a decreasing rate defined by the following differential equation:

$$- dC/dt = kC^n \quad [\text{Eq. 1}]$$

The differential term, dC/dt is the rate of carbon disappearance, C is the amount of carbon present per reacting volume at any instant, k is the rate constant or "reactivity," and n is the order of the reaction. The rate constant, k , is the accepted measure of reaction rate and roughly predicts whether the reaction can be practically carried out in a gasifier of reasonable size using a given feed at a temperature found to produce a desired gas mix. The rate constant is also the measure of relative effectiveness of different catalysts, either inherent, as lignite ash, or added, as mineral to the gasifier feed. That k varies over an extremely wide range for different coals, at the same temperature, is shown by Figure A-3.

A complicating factor is reaction order, n , determined from the slope of a plot of $\log dC/dt$ vs. $\log C$ and is an indication of the manner in which the rate of the reaction varies with the concentration of active carbon.

The solution to this equation, for the simple first order case where $n = 1$, is as follows:

$$C(t) = C_0 e^{-kt} \quad [\text{Eq. 2}]$$

This equation describes the steam-char reaction alone. However, both isothermal rate and equilibrium are affected by at least a dozen or so other reactions between the C , H_2O , CO , CO_2 , CH_4 , O_2 , N_2 (as a diluent), other light organics, and volatile tars (especially in the case of bituminous coals). Their net result on the reactions (1) above, is as follows:

Figure A-1. Thermogravimetric analyzer.

Figure A-2. Thermogravimetric analysis--typical data.

Figure A-3. Wt% carbon conversion versus time for two bituminous, one subbituminous, and three lignite coal chars at 750°C.

$$C(t) = C_0 / (C_0 k t + 1) \quad \text{for } n = 2 \quad [\text{Eq. 3}]$$

$$C(t) = C_0 - (k t / 2) C_0^{1/2} + k^2 t^2 / 4 \quad \text{for } n = 1/2 \quad [\text{Eq. 4}]$$

$$C(t) = C_0 - k t \quad \text{for } n = 0 \quad [\text{Eq. 5}]$$

There are rare documented cases of chemical reactions of ternary or higher order. Zeroth order is not uncommon, especially in surface reactions where there is a high degree of surface adsorption involved. In the gasification reaction, carried out in excess steam to suppress any rate control due to deficiency of water, formation of an intermediate activated complex may or may not be dependent on the carbon. If only selected carbons reach the activated state in the presence of adsorbed water, the order with respect to concentration of active carbon will have a nonzero value. If, however, the reaction occurs without dependence on active carbon since the concentration of activation sites may be taken as constant, the order of the reaction is zero with respect to carbon.

The above equations give reasonable approximations of k , although a much broader array of n values exist and can be determined. For a single set of $C(t)$ data, determination of k presents the problem of a single equation in two unknowns. Substituting n obtained from the plot described above enables k to be determined. However, on reducing TGA data, values of $n = 0.5, 1$ or 2 selected on the basis of agreement with experimental n generally give satisfactory matches between experimental data and theoretical curves making it unnecessary to use the precise value of n . In gasification of complex materials such as wood, coal, solid waste, etc., experience has shown that fine resolution (e.g., $n = .9$ or $n = 1.7$) is unnecessary since it implies greater than the experimental accuracy.

The thermogravimetric analyses (TGA) of the steam gasification reactions were carried out on a commercial 100 mg capacity DuPont 951 TGA module, shown in Figure A-1, interfaced to a DuPont 1090 thermoanalyzer data station. Selected experiments were repeated on a 10-gram capacity TGA built at EERC. The smaller scale kinetics experiments involved 30 to 50 milligrams (dependent on fineness of grind and wood density) of ground wood loaded on a sample pan under argon flowing at 160 cc/min. The temperature was raised to a predetermined target temperature of 700, 750 or 800°C at ~100°C/min. During this temperature increase, the sample was devolatilized, producing a char, and when the temperature reached the target, excess steam flow was introduced through a side arm into the sample chamber. The argon carrier flow was reduced to ~ 60 cc/min for the duration of the experiment. When the char weight reached < 50% of its original value, the experiment was terminated. Total gas effluent was collected in a gas bag for analysis by gas chromatography (GC). Weight, time, and temperature were automatically recorded at 2, 3, or 6 second intervals by the data station on a floppy disk for later processing. An example of data collected during one of the tests is shown in Figure A-2.

Another essential property of a reactive char is the energy of activation. Reaction rate is dependent on the number of atoms or molecules in the activated state. In gasification reactivity studies the activation of carbon controls the rate since the other reactant, steam, is in large excess and presumably contains an excess of activated steam molecules. Because the number of active sites is a function of temperature, increasing the

temperature increases the number of active carbons which in turn increases reaction rate. The char carbon reactivity in the absence of reaction control by mass transfer increases with increasing temperature allowing calculation of energy of activation according to the theory of Arrhenius:

$$d(\ln k)/dT = E/RT^2 \quad \text{or} \quad k = A e^{-E/RT} \quad [\text{Eq. 6}]$$

where k is the reactivity, A is the preexponential (frequency) factor, E is the energy of activation, T is absolute temperature ($^{\circ}\text{K}$) and R is the universal gas constant. The physical interpretation of the preexponential factor, A , which is also referred to as a frequency factor is not without some rigor. The solution as given by W.C. McC. Lewis (1) suggests that A is equal to the frequency of collisions between molecules for reactions of order > 1 in which case the application of the term frequency is intuitively obvious. For example, for a reaction between two molecules:

$$v = ze^{-E/RT} \quad \text{in molecules cc}^{-1} \text{ sec}^{-1} \quad [\text{Eq. 7}]$$

where z is the number of collisions per second in 1 cc of gas and is given by kinetic theory as

$$z = n_A n_B \sigma_{AB}^2 [8\pi KT((m_A + m_B)/m_A m_B)]^{1/2} \quad [\text{Eq. 8}]$$

n 's are the concentrations, σ_{AB} is the average molecular diameter, m_A and m_B are molecular masses, and K is the Boltzmann constant. Since

$$v = kn_A n_B \quad [\text{Eq. 9}]$$

and

$$k = \sigma_{AB}^2 [8\pi KT((m_A + m_B)/m_A m_B)]^{1/2} e^{-E/RT} \quad [\text{Eq. 10}]$$

then

$$k = Ze^{-E/RT} \quad [\text{Eq. 11}]$$

where Z is the collision number and for Arrhenius theory $Z = A$.

Energy of activation is calculated from the slope of a plot of $\ln k$ vs $1/T$ where the reaction is carried out at a minimum of three temperatures and where the rate of conversion is assumed to be described by Equation 2. The E 's measured in these experiments are apparent energies and, since they are dependent on heating rate (among other factors), are understood to be apparent procedural activation energies. The preexponential factor, A , is the intercept of the curve. The curve is linear when the reaction is under chemical control and non-linear Arrhenius plots may indicate a change in reaction mechanism or mass transfer control of the reaction.

The TGA method has become a routine procedure at EERC for rapid and inexpensive screening of large numbers of coals or woods, with and without catalysts over ranges of temperatures for rough approximation of their performance as gasifier feedstock. An on-going area of fundamental research is the determination of why different coals have widely different values of reactivity, k . All work at EERC supports the contention that the major factor in determining k is the concentration of active sites on the carbonaceous matrix, at which various catalytic cations (K^+ , Na^+ or Ca^{++} , for example) are or can be attached. Figure A-3 shows the effect of variations in intrinsic

catalysis for different coals, depending not only on the amount of catalytic elements present as ash, but on the extent to which they are organically bonded to active sites, as opposed to being in the form of stable mineral grains. Coals with a generous surplus of active sites are amenable to greatly enhanced reactivity by saturating the sites with mobile catalytic cations, either during the gasification reaction, as in the case of the TGA data of Figure A-4, or by prior chemical impregnation. The entire array of potentially practical combinations of coals, catalysts and gasification conditions approaches infinity. The value of TGA analysis is as a simple, minimal cost, screening step, to select candidate combinations for more detailed and costly testing, as indicated in Figure A-5.

Figure A-4. Effects of different catalysts on reactivity of Velva lignite.

Figure A-5. EERCs program sequence for evaluation of coal-catalyst-process candidates.

APPENDIX B

TWO EXAMPLES OF COMPLETE PRINTOUTS FOR ANALYSIS OF DATA FROM EERCS CONTINUOUS PROCESS UNIT (CPU), OPERATING IN THE GASIFICATION MODE

Examples presented: Run M-224 (KOH-impregnated Wyodak coal in limestone bed)
and Run M-233 (KOH-impregnated coal in taconite bed)

The first sheet in each set is a condensation of raw, on-line data generated by CPU operators. These data, plus laboratory analyses of all gas, solid, and (if desired) liquid products are inputs to Lotus file CPUDATA.WKI, which generates the minimum of five subsequent sheets.

	Gms In	Gms Out	Yields	M Yields
MAF (Coal/char)	1723.6	730.5	42.4	32.7
H2O in coal/Char	734.7	5.8	-42.3	-42.3
H2O in H2O/Cond.	3384.0	3429.9	2.7	18.5
Ash	821.7	1019.7	11.5	0.3
Sulfur	69.4	69.4	0.0	0.0
Ash(sulfur free)	752.3	950.3	11.5	0.3

1/9/92

Run # M233

i-Wyodak/Taconite

Temp. 650 C

Pressure 34.7 psia

Cond. Total	29.06	1.69	1.82
ibp-165	0.00	0.00	0.00
<C10	0.00	0.00	0.00
BXT	0.00	0.00	0.00
165-220	0.00	0.00	0.00
C10-C12	0.00	0.00	0.00
Phenols	0.00	0.00	0.00
Cresols	0.00	0.00	0.00
Naphthal.	0.00	0.00	0.00
220-375	0.00	0.00	0.00
C13-C22	0.00	0.00	0.00
C2-Phenol	0.00	0.00	0.00
Phytene	0.00	0.00	0.00
375-550	0.00	0.00	0.00
C23-C30	0.00	0.00	0.00
550-1000	0.00	0.00	0.00
Aliphatics	0.00	0.00	0.00
Phenolics	0.00	0.00	0.00
BP>1000	0.00	0.00	0.00
Char Fines	0.00	0.00	0.00
Residue	0.00	0.00	0.00

% H2O	28.4
% Ar	0.0
% N2	71.6
% NO	0.0
% CO2	0.0

					SCF
Gas Total	13245.2	16410.7	183.7	89.0	81.3
H2		124.7	7.2	6.5	48.5
CO2		1302.3	75.6	68.0	23.0
C3H8		0.0	0.0	0.0	0.0
C3H6		0.0	0.0	0.0	0.0
i-C4		0.0	0.0	0.0	0.0
COS		0.0	0.0	0.0	0.0
n-C4		0.0	0.0	0.0	0.0
H2S		0.0	0.0	0.0	0.0
1-Bu		0.0	0.0	0.0	0.0
t-2-Bu		0.0	0.0	0.0	0.0
i-C5		0.0	0.0	0.0	0.0
c-2-Bu		0.0	0.0	0.0	0.0
n-C5		0.0	0.0	0.0	0.0
C2H4		17.6	1.0	0.9	0.5
C2H6		18.9	1.1	1.0	0.5
O2	0.0	0.0	0.0	0.0	0.0
N2	13245.2	14723.0	85.7	0.9	0.5
CH4		100.8	5.8	5.3	4.9
CO		123.4	7.2	6.4	3.4
NH3		0.0	0.0	0.0	0.0

Total	19909.2	21625.7	199.6	100.0
-------	---------	---------	-------	-------

Mat. Balance	108.6
--------------	-------

% loss to char1	0
% loss to char2	21
% loss to liq	-16
% loss to gas	95

EERC CONTINUOUS PROCESS UNIT - RAW DATA SUMMARY.

PAGE 0

THIS PAGE: ALL DATA FROM MILDGAS PERSONNEL.

Spreadsheet last edited/revised: March 3, '92

RUN NO.: M-233

DATA SOURCE/USE CODE:

DATE: 12-12-91

R = RAW LABORATORY DATA SHEETS AND NOTEBOOK.

Entered: 3-28-92

M = MILDGAS MAT'L BAL NORMALIZATION SPREADSHEET.

A = ANALYSIS OF SAMPLE (PROX/ULT/XRFA/--), RPRTD P.1 OR 2.

I = CALCTD. INPUTS TO FOLLOWING PAGES. NR = NOT REPORTED.

	DATA ITEM	UNITS	REPORTED	CONVTD.
M	Coal		Wyodak	
R	Max. Particle Size.	inch.	0.25	6.35 mm
M	Bed Material		Taconite	
R	Max. Particle Size.	inch.	0.05	1.17 mm
R	Co-fed Catalyst		KOH	
M	Duration of run.	Hrs.	4.00	
M	Temperature	degC	650	1202 F
M	Pressure	PSIA	34.70	2.4 Atm
M	Coal Feed, MAF.	gms	1723.6	
I		Lb/Hr.		0.948
M	Moisture in Coal.	gms	734.7	22.4 %
M	Ash in Coal.	gms	821.7	25.1 %
I		Lb/Hr		0.452
I	Coal Feed, Raw/As Recvd.	gms	3280.0	
I		Lb/Hr		1.804
M	Sulfur.	gms	69.4	
M	Product Gas (Dry, N2-free).	SCF	81.3	98.2 %
I		SCFH		20
M	H2	SCF	48.5	59.7 %
M	CO	SCF	3.4	4.2 %
M	CO2	SCF	23.0	28.3 %
M	CH4	SCF	4.9	6.0 %
M	H2S	SCF	0.0	0.0 %
R	Bed Overflow Ash	gm	1434.0	
I		Lb/Hr		0.789
R	Fly Ash from Cyclone.	gm	322.0	
I		Lb/Hr		0.177
R	Condensate	gm	3459.0	
I	(Assume density of water)	Lb/Hr		1.902
M	Water In, as Steam.	gm	3384.0	
I		Lb/Hr		1.861
M	Nitrogen In.	gm	13245.0	
I		Lb/Hr		7.285
M	Total Water Out.	gm	3435.7	
I	Difference. *	% Input		-16.6 %
M	Nitrogen Out.	gm	14723.0	
I	Difference. *	% Input		11.2 %

Reflects leakage &/or inaccuracy of water and gas flow measurement, before normalization of product gas flow.

PAGE 1

```
>>>>>>>>> INPUT DATA BLOCK <<<<<<<<<<<<
```

B-3

RUN NO.: M-233

>>>>>>>>>>>>

Volatile matter balance
on next page.

VOLATILE MATTER
 VM in: 0.49 LB/HR
 VM out. Cyclone: 0.03 LB/HR
 Overflow: 0.06 LB/HR
 Total: 0.09 LB/HR
 TOTAL VM CONSUMED: 0.40 LB/HR
 % OF FEED: 81 %

```
=====
Wt. Fraction Calculation
Avg. Mol. Wt.: 16.22      Mol %      Wt. %
Density, Lb/SCF: 0.0419  H2         60      1.20    7.41
BTU/Lb.          CO         4        1.18    7.25
  Calculated here = 6589    CO2        29     12.63   77.85
  From Lab. Anal. = 6265    CH4         6       0.94    5.82
BTU/SCF=          H2S         0        0.00    0.00
Production, SCFH = 20.33    C2/C2+ *    1       0.27    1.66
      Lb/Hr =       0.85
Total              100      16.22 100.00
* All C2/C2+ assumed C2H6, if < 1%.
```

Wt. % C in Gas = 30.04 %
 WT. C OUT AS GAS = 0.26 Lb/Hr
 TOTAL C IN FEED = 0.68 Lb/Hr -- Based on C in Ult. Anal.
 C--> Gas Convrns.= 37.71 % -- incl. both FC and VM sources.
 FC consumed = 0.34 Lb/Hr,

CARBON BALANCE.
 C OUT, CYCLONE: 0.031 Lb/Hr
 C OUT, OVERFLOW: 0.349 Lb/Hr
 C ACCOUNTED FOR: 93.6 %

```
=====
REPORTED PROBABLE WEIGHT OF BED MATERIAL.      | BED DIMENSIONS
LOW      HIGH      | Dia. = 3 "
2000.00 g 2256.00 g | Ht. = 30 "
4.41 Lb  4.97 Lb   | A, Ft^2: 0.05
                  | Ft^3 = 0.12
                  | Liters = 1.39
FIXED CARBON IN BED: 1.34 Lb  1.51 Lb | -----
                              = C, Lb
```

-dC/dt (Lb/Hr) = kC, ASSUMING 1st ORDER (n = 1), = 0.34 Lb/Hr

REACTIVITY, k = (dC/dt)/C =
 LOW: 0.257 1/Hr
 HIGH: 0.228 1/Hr
 AVG.: 0.242 1/Hr

EERC CONTINUOUS PROCESS UNIT.
 RUN SUMMARY SHEET

RUN NO. M-233
 DATE: 11-19-91

RUN SPECIFICATIONS.

Coal Feed:	Wyodak	Top Size=	6.35 mm
Bed Material:	Taconite	Top Size=	1.17 mm
Bed Make-up Rate:	20 % of Feed.		
Co-fed Catalyst:	KOH		
	4 % of Feed.	K/FC=	0.02 Mol/Mol
TEMPERATURE:	650 degC	H2O/FC:	2.11 Mol/Mol
	1202 degF		
PRESSURE:	34.7 PSIA	DURATION	4.0 Hours
	2.4 Atm	SHUT-DOWN	Planned.

COAL FEED.

Moisture (Raw):	28.60 %	Feed, Raw	1.80 Lb/Hr
Ash (Raw):	4.90 %	Feed, MAF	0.95 Lb/Hr
Volatiles, MAF:	48.60 %	MAF Convrted.:	71.12 %
FC, MAF:	51.40 %	FC Convrted.:	58.63 % (1)

PRODUCT GAS (Normalized Mol. %).

H2	60.10 %		
CO	4.20 %	Gas Yield Summary:	Lb/Lb
CO2	28.70 %	Wt. Gas/MAF Feed:	0.90
CH4	5.90 %	Wt. Gas/FC Consumed:	2.47
H2S	0.00 %	Wt. H2/MAF Feed:	0.07
C2/C2+	0.90 %	Wt. H2/FC Consumed:	0.18
	-----%	Wt. CH4/MAF Feed:	0.05
Total	99.80 %	Wt. CH4/FC Consumed:	0.14

BTU/SCF: 276

EFFECTIVE REACTIVITY:

0.242 1/Hr

Volumetric Throughput Capacity =

2.81 Lb/Hr-Ft³

(1) If bed expanded 0.123 to 0.199 Ft³, to achieve 95% FC
 conversion, vol. capacity would = 1.73 Lb/Hr-Ft³

ACCURACY/VALIDITY.

Input N2 accounted for:	111.2 % (2)
Input water accounted for:	83.4 %
Input Ash accounted for:	124.7 %
Input Carbon accounted for:	93.6 %

(2) As-measured raw gas flow adjusted to make this closure = 100%
 to establish "normalized" product gas flow.

	Gms In	Gms Out	Yields	N Yields	
MAF (Coal/char)	1867.9	875.0	46.8	41.3	2/5/92
H2O in coal/Char	790.5	2.0	-42.2	-42.2	
H2O in H2O/Cond.	3276.2	2639.6	-34.1	-11.9	Run # M224
Ash	621.6	705.0	4.5	0.0	i-Wyodak/Limest
Sulfur	67.8	67.8	0.0	0.0	Temp. 700
Ash(sulfur free)	553.8	637.1	4.5	0.0	Pressure 89.7

Cond. Total	22.40	1.20	1.39	% H2O	11.6
ibp-165	0.00	0.00	0.00	% Ar	0.0
<C10	0.00	0.00	0.00	% H2	88.4
BXT	0.00	0.00	0.00	% NO	0.0
165-220	0.00	0.00	0.00	% CO2	0.0
C10-C12	0.00	0.00	0.00		
Phenols	0.00	0.00	0.00		
Cresols	0.00	0.00	0.00		
Naphthal.	0.00	0.00	0.00		
220-375	0.00	0.00	0.00		
C13-C22	0.00	0.00	0.00		
C2-Phenol	0.00	0.00	0.00		
Phytene	0.00	0.00	0.00		
375-550	0.00	0.00	0.00		
C23-C30	0.00	0.00	0.00		
550-1000	0.00	0.00	0.00		
Aliphatics	0.00	0.00	0.00		
Phenolics	0.00	0.00	0.00		
BP>1000	0.00	0.00	0.00		
Char Fines	0.00	0.00	0.00		
Residue	0.00	0.00	0.00		

					SCF
Gas Total	38956.0	45902.8	371.9	101.5	110.9
H2		181.2	9.7	8.6	69.6
CO2		1504.2	80.5	71.7	26.3
C3H8		0.0	0.0	0.0	0.0
C3H6		0.0	0.0	0.0	0.0
i-C4		0.0	0.0	0.0	0.0
COS		0.0	0.0	0.0	0.0
n-C4		0.0	0.0	0.0	0.0
H2S		0.0	0.0	0.0	0.0
1-Bu		0.0	0.0	0.0	0.0
t-2-Bu		0.0	0.0	0.0	0.0
i-C5		0.0	0.0	0.0	0.0
c-2-Bu		0.0	0.0	0.0	0.0
n-C5		0.0	0.0	0.0	0.0
C2H4		0.0	0.0	0.0	0.0
C2H6		0.0	0.0	0.0	0.0
O2	0.0	0.0	0.0	0.0	0.0
N2	38956.0	43793.5	259.0	1.0	0.6
CH4		136.7	7.3	6.5	6.6
CO		287.2	15.4	13.7	7.9
NH3		0.0	0.0	0.0	0.0
Total	45512.2	50146.8	348.1	90.1	

Mat. Balance 110.2

% loss to char1 0
 % loss to char2 4
 % loss to liq -9
 % loss to gas 109

EERC CONTINUOUS PROCESS UNIT - RAW DATA SUMMARY.

PAGE 0

THIS PAGE: ALL DATA FROM MILDGAS PERSONNEL.

Spreadsheet last edited/revised: March 3, '92

RUN NO.: M-224

DATA SOURCE/USE CODE:

DATE: 12-9-91

R = RAW LABORATORY DATA SHEETS AND NOTEBOOK.

Entered: 3-9-92

M = MILDGAS MAT'L BAL NORMALIZATION SPREADSHEET.

A = ANALYSIS OF SAMPLE (PROX/ULT/XRFA/--), RPRTD P.1 OR 2.

I = CALCTD. INPUTS TO FOLLOWING PAGES. NR = NOT REPORTED.

	DATA ITEM	UNITS	REPORTED	CONVTD.
M	Coal		Wyodak Subbt.	
R	Max. Particle Size.	inch.	0.25	6.35 mm
M	Bed Material		Limestone	
R	Max. Particle Size.	inch.	0.07	1.65 mm
R	Impregnated Catalyst		KOH	
R	Duration of run.	Hrs.	4.00	
M	Temperature	degC	700	1292 F
M	Pressure	PSIA	90	6.1 Atm
M	Coal Feed, MAF.	gms	1862.9	
I		Lb/Hr.		1.025
M	Moisture in Coal.	gms	790.5	24.1 %
M	Ash in Coal.	gms	621.6	19.0 %
I		Lb/Hr		0.342
I	Coal Feed, Raw/As Recvd.	gms	3275.0	
I		Lb/Hr		1.801
M	Sulfur.	gms	67.8	
M	Product Gas (Dry, N2-free).	SCF	110.9	99.5 %
I		SCFH		28
M	H2	SCF	69.6	62.8 %
M	CO	SCF	7.9	7.1 %
M	CO2	SCF	26.3	23.7 %
M	CH4	SCF	6.6	6.0 %
M	H2S	SCF	0.0	0.0 %
R	Bed Overflow Ash	gm	745	
I		Lb/Hr		0.229
R	Fly Ash from Cyclone.	gm	416.0	
I		Lb/Hr		0.229
R	Condensate	gm	2662.0	
I	(Assume density of water)	Lb/Hr		1.464
M	Water In, as Steam.	gm	3276.2	
I		Lb/Hr		1.802
M	Nitrogen In.	gm	38956.0	
I		Lb/Hr		21.426
M	Total Water Out.	gm	2641.6	
I	Difference. *	% Input		-35.0 %
M	Nitrogen Out.	gm	43793.5	
I	Difference. *	% Input		12.4 %

* Reflects leakage &/or inaccuracy of water and gas flow measurement, before normalization of product gas flow.

```
>>>>>>>>>> INPUT DATA BLOCK <<<<<<<<<<<<<<
```

B-9

>>>>> SOLIDS ANALYSIS INPUT DATA <<<<<<

B-10

VOLATILE MATTER
 VM in: 0.53 LB/HR
 VM out. Cyclone: 0.02 LB/HR
 Overflow: 0.28 LB/HR
 Total: 0.31 LB/HR
 TOTAL VM CONSUMED: 0.22 LB/HR
 % of Feed: 42 %

=====

GAS CALCULATIONS.

		Wt. Fraction Calculation			
			Mol %		Wt. %
Avg. Mol. Wt.:	14.58	H2	64	1.28	8.76
Density, Lb/SCF:	0.0377	CO	5	1.49	10.24
BTU/Lb.		CO2	25	10.81	74.15
Calculated here =	7433	CH4	6	1.00	6.86
From Lab. Anal. =	6265	H2S	0	0.00	0.00
BTU/SCF=	280	C2/C2+ *	0	0.00	0.00
Production, SCFH =	27.73	-----			
Lb/Hr =	1.05	Total	100	14.58	100.00
		* All C2/C2+ assumed C2H6, if < 1%			

Wt. % C in Gas = 29.75 %
 WT. C OUT AS GAS = 0.31 Lb/Hr
 TOTAL C IN FEED = 0.66 Lb/Hr -- Based on C in Ult. Anal.
 C--> Gas Convrsn.= 47.43 % -- incl. both FC and VM sources.
 FC consumed = 0.12 Lb/Hr
 Wt. VM Consumed = 0.22 Lb/Hr

CARBON BALANCE.

C OUT, CYCLONE: 0.035 Lb/Hr
 C OUT, OVERFLOW: 0.278 Lb/Hr
 C ACCOUNTED FOR: 95.1 %

=====

		BED DIMENSIONS	
REPORTED PROBABLE WEIGHT OF BED MATERIAL.		Dia. =	3
LOW HIGH		Ht. =	30
		A, Ft^2:	0.05
2000.00 g 2256.00 g		Ft^3 =	0.12
4.41 Lb 4.97 Lb		Liters =	1.39
FIXED CARBON IN BED:	0.82 Lb 0.92 Lb	-----	

-dC/dt (Lb/Hr) = kC, ASSUMING 1st ORDER (n = 1), = 0.36 Lb/Hr
 REACTIVITY, 1 = (dC/dt)/C =
 ("C" = FC) LOW: 0.445 1/Hr
 HIGH: 0.394 1/Hr
 AVG.: 0.420 1/Hr

EERC CONTINUOUS PROCESS UNIT.

RUN NO. M-224

RUN SUMMARY SHEET

DATE: 11-19-91

RUN SPECIFICATIONS.

Coal Feed:	Wyodak Subbt.	Top Size=	6.35 mm
Bed Material:	Limestone	Top Size=	1.65 mm
Bed Make-up Rate:	20 % of Feed.		
Co-fed Catalyst:	KOH		
	4 % of Feed.	K/FC=	0.10 Mol/Mol

TEMPERATURE:	700 degC	H ₂ O/FC:	2.30 Mol/Mol
	1292 degF		

PRESSURE:	89.7 PSIA	DURATION	4.0 Hours
	6.1 Atm	SHUT-DOWN	Planned.

COAL FEED.

Moisture (Raw):	28.60 %	Feed, Raw	1.80 Lb/Hr
Ash (Raw):	4.90 %	Feed, MAF	1.02 Lb/Hr
Volatiles, MAF:	48.60 %	MAF Convrted.:	64.70 %
FC, MAF:	51.40 %	FC Convrted.:	69.43 % (1)

PRODUCT GAS (Normalized Mol. %).

H ₂	63.86 %		
CO	5.33 %	Gas Yield Summary:	Lb/Lb
CO ₂	24.57 %	Wt. Gas/MAF Feed:	1.02
CH ₄	6.25 %	Wt. Gas/FC Consumed:	2.88
H ₂ S	0.00 %	Wt. H ₂ /MAF Feed:	0.09
C ₂ /C ₂ +	0.00 %	Wt. H ₂ /FC Consumed:	0.25
	-----%	Wt. CH ₄ /MAF Feed:	0.07
Total	100.01 %	Wt. CH ₄ /FC Consumed:	0.20

BTU/SCF: 280

EFFECTIVE REACTIVITY:

0.420 1/Hr

Volumetric Throughput Capacity = 2.96 Lb/Hr-Ft³

(1) If bed expanded 0.123 to 0.168 Ft³, to achieve 95% FC conversion, vol. capacity would = 2.16 Lb/Hr-Ft³

ACCURACY/VALIDITY.

Input N ₂ accounted for:	112.4 % (2)
Input water accounted for:	65.0 %
Input Ash accounted for:	113.5 %
Input Carbon accounted for:	95.1 %

(2) As-measured raw gas flow adjusted to make this closure = 100% to establish "normalized" product gas flow.

6.2 Sulfur Forms in Coal

SULFUR FORMS IN COAL

**Semiannual Technical Progress Report
for the Period January 1, 1992, to June 30, 1992**

by

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SULFUR FORMS IN COAL

1.0 INTRODUCTION

The accurate and precise analysis of a solid material, such as coal, requires that the analytical method utilize energy, solvent, or reagent that can effectively permeate the matrix and contact the element of interest. Physicochemical barriers preventing such contact have proven formidable when sulfur analysis of solid coal by conventional technologies is attempted. Analysis of coal for sulfur by volatilization of sulfur moieties is limited by their volatilities and vapor transport through the matrix, and liquid extraction of those moieties is limited by conventional solubility and permeability. Chemical derivatization for ^{13}C nuclear magnetic resonance (NMR) spectroscopy is reagent-transport limited, ^{33}S NMR is limited by absorption bandwidth, and x-ray techniques are limited to surface analysis by the inability to penetrate the solid more than a few angstroms. Given these drawbacks, a technique that would allow solvent penetration into the entire sample and dissolution of the sulfur species, with the ability to obtain those species intact in a form that can be identified and quantified by conventional analytical methods, would advance sulfur science immeasurably.

A method that has potential for providing the desired improvement is supercritical fluid extraction (SFE). SFE as a separations method is superior to the other extraction methods, including Soxhlet extraction. Because of the relatively poor mass transfer in liquids, liquid solvent extractions are inherently slow. Compared to liquid solvents, supercritical fluids have several characteristics that make them attractive extraction solvents, as well as media for selective reactions. First, supercritical fluids have solvent strengths similar to those of liquid solvents but, in contrast to liquid solvents, they have lower viscosities (10^{-4} versus 10^{-3} N-sec/ m^2) and higher solute diffusivities (10^{-4} versus 10^{-5} cm^2/sec), which greatly improve mass transfer and greatly reduce the time for quantitative extractions (and reactions) to be performed. Second, the polarity of a supercritical fluid changes with its density as described by several correlations (1-3), including the simple empirical correlation proposed by Giddings and others (4): $\delta = 1.25 P_c^{1/2}(\rho/\rho_l)$ where δ is the Hildebrand solubility parameter, P_c is the critical pressure of the fluid, ρ is the density of the supercritical fluid, and ρ_l is the density of the fluid in its liquid state. As shown by these correlations, the selectivity of a supercritical fluid for a target analyte can be optimized by simply controlling the extraction pressure (and to a lesser extent, the temperature). Supercritical fluids are also available that have widely varying polarities ranging from low-polarity fluids (e.g., ethane) to moderately polar fluids (e.g., CO_2) to polar fluids (e.g., water, although not to be construed to be as polar as liquid water), which, along with pressure and temperature control, give the analyst an extremely wide range of extraction solvent polarities to perform selective extractions. Third, in contrast to popular belief, analytical-scale (not process-scale) supercritical fluid extractions are experimentally simple and inexpensive to perform.

2.0 OBJECTIVES

The overall objective of this project is to develop methodology which will enable the rapid and accurate identification and quantitation of sulfur

species in what is now referred to as the "organic" sulfur component of coal. To accomplish this, the following specific objectives must be met:

- To investigate and develop the use of SFE and pyrolysis/SFE (PYR/SFE) for the selective extraction of organic forms from coal
- To identify and quantitate the individual sulfur organics recovered using SFE procedures
- To investigate and develop the use of selective pyrolysis and/or chemical oxidation/reduction for the determination of organic sulfur forms in coal
- To evaluate and incorporate other promising sulfur speciation techniques

3.0 MATERIALS, EQUIPMENT, AND METHODS DESCRIPTIONS

3.1 Coal Characterization

Table 1 contains the proximate and total sulfur analyses of the test coals used in the sulfur analysis experiments this quarter. Well-characterized coals from the Illinois Basin coal sample program, (IBCSP) were supplied by the Illinois State Geological Survey. The proximate analyses of these coals, reported in Table 1, are those most recently obtained at the EERC. The sulfur analyses include results sent from the IBC sample program with the samples, results obtained from the Energy and Environmental Research Center (EERC) laboratory, and results obtained from an independent commercial laboratory, Minnesota Valley Testing Laboratory (MVTL). Table 2 contains the ASTM sulfur forms analyses results on the same coals. Although some of these values appeared in the previous quarterly report, they are included here again for the convenience of the interested reader. Most of the work in this semiannual period was carried out with IBC-101, some with IBC-102, and only selected tests with the remainder of the coals.

3.2 Experimental Apparatus and Materials

A description of the basic apparatus used in the SF extraction experiments is given in the July through September 1990 quarterly report (5). Figure 1 is a schematic of the SFE equipment currently in use, including the gas chromatography (GC) oven used to heat the cell during PYR/SFE experiments. Figure 2 shows a schematic of SFE equipment used in performing on-line analysis of SF extracts. Modifications to the previous apparatus include the use of commercial extraction cells purchased from Keystone™ and the replacement of the fused silica restrictor with the heated stainless steel restrictor. The latter had the constriction near the center of the tube rather than at the end, making the constriction easier to keep hot while still delivering the effluent into the collection solvent. The Keystone™ cells have been successfully used at temperatures of 450°C at 400 atm. (This does not imply endorsement of this company and should not be construed as a recommendation of these cells for SFE use. Identification is for information purposes only.) All other equipment used in this study was common laboratory equipment.

TABLE 1

Proximate and Sulfur Analyses of SFE Test Coals

Coal Samples (IBC):	101	102	106	107
Moisture	10.20	8.28	6.41	5.31
Volatile Matter	36.12	35.75	37.03	37.51
Fixed Carbon	44.69	50.90	48.82	46.01
Residue	9.01	5.08	7.72	11.19
Total Sulfur: EERC	4.13	3.35	3.53	3.54
IBCSP	4.36	3.30	3.77	3.72
MVTL	4.44	3.27	3.68	3.59

EERC: Total sulfur values determined by the EERC.

IBCSP: Total sulfur values determined by the Illinois Basin coal sample program.

MVTL: Total sulfur values determined by MVTL Laboratories, Inc., Bismarck, ND.

TABLE 2

Sulfur Forms Analyses of Coal Samples Used in This Work

IBC	101	102	106	107
<u>Sulfatic Sulfur</u>				
a	0.05	0.06	0.01	0.26
b	0.67	1.17	0.73	0.37
c	0.07	0.16	0.11	0.29
<u>Pyritic Sulfur</u>				
a	1.22	2.26	1.86	0.48
b	0.53	0.61	0.72	0.42
c	1.09	1.66	1.50	0.51
<u>Organic Sulfur</u>				
a	3.08	0.98	1.90	2.98
b	3.24	1.48	2.24	2.80
c	1.09	1.58	2.29	2.76
<u>Total Sulfur</u>				
a	4.36	3.30	3.77	3.72
b	4.44	3.27	3.68	3.59
c	4.53	3.41	3.90	3.55
d	4.13	3.35	3.53	3.54

a. Data from IBCSP.

b. MVTL Laboratories, Inc., Bismarck, ND (12/9/91).

c. MVTL Laboratories, Inc., Bismarck, ND (9/21/90).

d. EERC.

Figure 1. Schematic diagram of the SFE system outfitted for PYR/SFE.

Figure 2. Schematic diagram of the SFE system outfitted for PYR/SFE/cryogenic trapping/GC/MS, atomic emission detection, and SCD.

Bottled carbon dioxide containing 10% methanol was prepared by Scott Specialty Gas Company and was used directly from the bottle during SFE.

3.3 Methods

3.3.1 Supercritical Methanol-Modified CO₂ Extraction of Sulfur From Coal at Low Temperature

Extraction of elemental sulfur from coal has generally been more successful with methanol-modified SF CO₂ than with pure SF CO₂ at 110°C and 400 atm with 10% methanol/CO₂ (6). Eluted SF extracts were collected in ca. 2 mL of toluene for later analysis as previously described (5). Benzothiazole was added to each extract as an internal standard, and samples of each were transferred to septum vials. Analyses of these samples were obtained using a Hewlett-Packard 5890 GC with a Hewlett-Packard element-selective atomic emission detector (AED). Carbon and sulfur emissions were monitored simultaneously at 193 and 181 nm, respectively. Individual component IDs were obtained from a Hewlett-Packard 5985B GC/mass spectrometer (GC/MS).

3.3.2 Extraction With Supercritical Water

The apparatus shown in Figure 1 was used to extract IBC-101 with supercritical water at 450°C and 400 atm. The pump used was an Isco model μ LC 500, and the water was HPLC-grade water from Fisher Scientific Company. The collection solvent was HPLC-grade water.

3.3.3 Acid Extraction of Sulfur From Coal

Inorganic sulfur extraction from coal with HNO₃ was carried out according to the Riley Method (7). Extraction of sulfatic sulfur was a hydrochloric acid extraction adapted from ASTM method D2492-90.

3.3.4 On-Line PYR/SFE

IBC-101 coal ground to pass 200 mesh was preextracted with 10% methanol/CO₂ at 110°C and 400 atm for 100 minutes to remove elemental sulfur. The extraction was continued for an additional 100 minutes with pure CO₂ at 110°C and 400 atm to remove traces of methanol and soluble organics. One milligram of this preextracted coal was extracted at 450°C with 400 atm CO₂ for 10 minutes while the extract was collected in a -50°C cryogenic trap and subsequently analyzed by GC/MS. The experiment was repeated using AED detection in place of MS.

4.0 ACCOMPLISHMENTS

The accomplishments for the 6-month period beginning January 1, 1992, and ending June 30, 1992, are reported by task. Therefore, Section 4.1 reports Task A, 4.2 reports Task B, and 4.3 reports Task C.

4.1 Task A. Selective Supercritical Fluid Extraction

The major objective of this study is to develop rapid, reliable, but relatively simple, methods for the direct determination of each of the forms of sulfur in coal. As a result of the current work, a procedure for the

direct measurement of one of those forms, i.e., elemental sulfur, has been developed. Thus two of the forms of sulfur in coal can now be measured directly. The ASTM method (D2492-90) of analyzing coal for sulfatic sulfur already exists and is a satisfactory and reliable direct technique. The recently developed method for analyzing coal for elemental sulfur, besides being rapid, simple, and direct, produces little waste as a disposal concern. The technique has as its basis a nominal 30-minute supercritical 10% methanol/ CO_2 extraction at 400 atm and 110°C temperature. This method and its development are described in an article which has been reviewed and accepted for publication in *Fuel*. The article, whose title occurs in Section 5.0 Presentations and Publications below, describes the method in detail.

4.2 Task B. Selective Chemical and Thermal Extractions

Sulfur removal from coal at low and elevated temperatures by extraction with supercritical CO_2 was described previously (5, 6). The suite of temperatures used included the range 40°-450°C for varying time periods. The current work included extraction with 10% methanol/ CO_2 at 110° and 450°C.

4.2.1 PYR/SFE of Swelling Coal

Under pyrolysis conditions, IBC-101 softens and swells, resulting in reduced fluid-coal contact and the potential for SF-flow stoppage. To alleviate this problem, an accurately weighed amount of coal was mixed with washed sand and then extracted. The entire residue was analyzed for total sulfur after extraction. The percentage sulfur removal was then readily calculated:

$$1 - \frac{\text{Mass Sulfur in Residue After Extraction}}{\text{Mass Sulfur in Original Mass of Coal Sample}} \times 100 = \% \text{ S Removal}$$

Figure 3 shows the calibration curve obtained from a plot of milligrams of total sulfur measured versus milligrams of IBC-101 mixed with an equal quantity of sand for absolute total sulfur determination.

4.2.2 Effect of Chemical Reactants on SFE of Sulfur

Methods of removal of sulfur tested included SFE of IBC-101 under mild pyrolysis conditions with and without the presence of chemical reagents. Dynamic extractions with supercritical CO_2 at 400 atm and 450°C in the absence of a chemical reactant was successful in removing nearly 50 wt% of the sulfur from the coal, while supercritical 10% methanol/ CO_2 extraction under the same conditions was successful in removing nearly 60 wt% of the sulfur from the coal (Figure 4). SFE of IBC-101 containing 50 wt% added NaOH at the same conditions as above resulted in sulfur removals of slightly more than 50 wt% for each of the fluids. Dynamic SFE of 50 mg of IBC-101 spiked with 200 μL of 85% H_3PO_4 under the same conditions as the above resulted in >60 wt% sulfur reduction when extracted with 10% methanol/ CO_2 and 85 wt% reduction of S when extracted with CO_2 . H_3PO_4 solubility in SF 10% methanol/ CO_2 was greater than in SF CO_2 as evidenced by the amount of H_3PO_4 in the extract. Therefore, the residence time of the acid in the reaction cell during a dynamic extraction was significantly shorter in the methanol/ CO_2 extraction, allowing for shorter reaction time and accounting for reduced sulfur removal.

Figure 3. A sulfur standard calibration curve for LECO determination of total sulfur in 100% of a coal/sand-extracted mixture.

Extraction of coal with supercritical water has several attractive aspects. Included in the list of attractive features are the environmental acceptability of water, the polar nature (although not nearly the polarity of the liquid) of water as a SF with respect to other commonly used fluids, the variety of modifiers available for use with water, the specific heat capacity of SF water, and the cost of the water. At the test conditions of the initial supercritical water extraction of IBC-101, >50% by weight of the sulfur, as measured on an absolute scale as shown in Figure 4, was extracted. Additional extractions and extraction strategies with SF water are planned.

4.2.3 High-Temperature On-Line Extraction

Initial results utilizing on-line PYR/SFE/cryogenic trapping/GC with the MS as a detector to analyze elemental sulfur-free IBC-101 are shown in Figure 5. This technique reduces loss of sulfur compounds normally encountered in the solvent-trapping procedure which allows the more volatile of the major gas-chromatographable species to be identified. The total ion chromatogram shows all gas-chromatographable components detected by the MS rather than only the desired sulfur compounds. Figure 6 shows the AED chromatograms of carbon-containing species (top) and sulfur-containing species (bottom). Correlation of peaks in the bottom chromatogram with those of the top show which

Figure 4. Sulfur removal from IBC-101 at 450°C and 400 atm by CO₂ and 10% methanol/CO₂ with/without reagents.

Figure 5. Chromatogram of extract from PYR/SFE/GC/MS.

Figure 6. A typical GC-AED chromatogram of an SFE coal extract (IBC-101) showing the carbon (193 nm) and sulfur (181 nm) channels displayed.

components are true organosulfur compounds. The AED information enables the sorting of peaks in the total ion chromatogram of the MS, allowing identification of individual sulfur compounds in the extract.

Additional IBC-101 bituminous coal was then extracted with supercritical 10% methanol/CO₂ at 400 atm to remove elemental sulfur. Several fractions of the elemental-sulfur-free IBC-101 were then extracted using the on-line method recently developed. Figure 7 shows a total ion chromatogram of extract collected by cryogenic trapping during pyrolysis at 450°C. Selected ion-current chromatograms on the same figure show the C₁-C₅ thiophenes which make up a large portion of the volatile species.

Several additional sulfur compounds along with benzene, phenol, toluene, indan, indene, and other polynuclear aromatics are identified on Figure 8. Again the thiophenes are identified, but ethylene sulfide, benzo[b]thiophene, dibenzothiophene, and thianthrene are also prominent peaks in this chromatogram.

To gain additional information on the distribution of sulfur forms in coal, an extraction scheme was devised which enables the individual quantitative determination of elemental, sulfatic, other inorganic and true organic sulfur. It consists of SFE of elemental sulfur, HCl extraction of sulfatic sulfur from raw and elemental-sulfur-free coal, HNO₃ extraction of total inorganic sulfur from raw and elemental-sulfur-free coal, and true organic sulfur of residue on elemental-sulfur-free, acid-extracted coal. The scheme is shown in Figure 9 and will be evaluated in future work.

4.3 Task C. Other More Conventional Methods of Analysis

4.3.1 Sample Preparation for Stable Sulfur Isotope Experiments and Background Information Related to This Work

The results of sulfur forms analysis shown in Table 2 indicate that sulfatic sulfur increases on prolonged (>6 months) exposure to air. The pathway followed by the sulfur seems to be by way of pyritic sulfur oxidation, as also indicated by Table 2. A method of investigating the pathway has been designed using a coal (IBC-107) that has a natural sulfur probe, i.e., unusually high levels of stable ³⁴S isotope, and is described below. The high ³⁴S/³²S in the original coal and in the residue from acid-extracted IBC-107 makes them excellent candidates for testing the potential for organic and pyritic sulfur conversion to elemental sulfur.

Coal IBC-107 was selected for stable sulfur isotope analysis because of the large isotopic difference of ~22 ‰, between pyritic and organic sulfur (8). Because of this large isotopic difference, sulfur isotopic determination on the elemental sulfur obtained selectively by SFE may be applied to resolve the source of elemental sulfur in coal. A schematic description of the extraction scheme used in this study is depicted in Figure 10. Initially, two portions of ~4.5-g IBC-107 (~200 mesh size) coal were extracted with SF 10% methanol in CO₂ in a 10-mL Keystone extraction cell fitted with a stainless steel restrictor for 2 hours. An additional 15-min extraction was performed during which no elemental sulfur was extracted as determined by GC-AED. The large coal sample sizes extracted were necessary in order to obtain a sufficient quantity (~4 mg) of elemental sulfur for isotopic determination. About half of the SF-extracted coal was extracted with nitric acid (7) to

Figure 7. Total ion and selected ion chromatograms of extract from PYR/SFE/
GC/MS of IBC-101.

Figure 8. Total ion chromatogram (shown in three parts) of extract from PYR/SFE/GC/MS of IBC-101 with several major peaks identified.

Figure 9. Flow diagram of the differential extraction of sulfur forms from coal.

collect the pyritic and sulfatic sulfur from the coal. Another portion of the SF-extracted coal was extracted by the Canfield technique (9) to obtain the pyritic sulfur in coal. Stable sulfur isotope determinations were performed on the seven coal extracts and residues by an experienced research group headed by Professor Simon Bottrell in Leeds, UK, using an established procedure with stable sulfur isotope MS. In addition, total sulfur determination on all the five solid residues were carried out. Data from the stable isotope determinations coupled with the total sulfur values of the five solid residues and original coal samples provided information regarding sulfur forms transformation mechanisms in the coal matrix, which should lead back to the original source of elemental sulfur in coal. Table 3 shows the data obtained from the stable sulfur isotope analyses.

The analytical values for organic sulfur in the residues following Riley and Canfield extractions were identical within the precision of the isotope measurement. The analyses of the inorganic sulfur fraction collected during each of the extractions are not the same, but the difference is easily explained. Whereas the Canfield method liberates sulfur as H_2S exclusively from metallic sulfides, the Riley method oxidizes metallic sulfides to sulfates which cannot be separated from inherent sulfate. The Canfield method, then, gives what is expected to be a more accurate estimate of pyritic sulfur by measuring the isotope ratio in the liberated H_2S , while the inorganic sulfur in the Riley extract is determined from the total sulfate. In samples with low sulfate, the latter measurement fairly represents the pyritic sulfur, whereas in samples with high sulfate levels, the sulfur in the Riley extract is interpreted as inorganic, but not exclusively pyritic, sulfur.

Figure 10. Flow diagram of sample preparation for stable sulfur isotope analysis.

TABLE 3

Sample	Preparation	$\delta^{34}\text{S}_{\text{CDT}}$	Error (%)
PL-1	Parr bomb oxidation of total coal	+6.5	± 0.2
PL-2	Parr bomb oxidation of S_8 in SF extract collected in toluene	+13.4	± 0.2
PL-3x	Pyrite sulfur extracted from PL-3 by acidic chromous chloride (Canfield method)	+26.4	± 0.4
PL-3r	Organic S (residue from Canfield extraction) by Parr bomb oxidation	+1.6	± 0.2
PL-4	Inorganic S in Riley* extract of PL-3	+12.1	± 0.2
PL-5	Organic S (residue from Riley extraction) by Parr bomb oxidation	+1.5	± 0.2

* Boiling 2 N HNO_3 for 30 minutes.

Table 3 shows that the Riley acid extraction and the Canfield extraction separate the coal sulfur into fractions having nearly identical organic $^{34}\text{S}/^{32}\text{S}$ isotope ratios. The organic, pyritic, and total sulfur ratios compare favorably with those of other researchers (10). Interpretation of the data shown in Table 3 suggests that the elemental sulfur (PL-2) is related to the inorganic sulfur, but is inconclusive as to whether the relationship is exclusive; i.e., the argument can also be made that both inorganic and organic sulfur contribute to the formation of elemental sulfur.

To expand on the above findings, two additional coals, IBC-102 and IBC-106, were prepared for sulfur stable isotope analysis. The preparation included SFE to collect the elemental sulfur from the coal and Riley extraction to remove inorganic sulfur from the SF-extracted residue. The Canfield extraction is carried out on the SF-extracted residue at the Stable Isotope Laboratory. These samples, along with raw coal, were sent to the Stable Isotope Analysis group in Leeds, UK, for analysis at no charge to the EERC.

5.0 PRESENTATIONS AND PUBLICATIONS

1. Louie, P.K.K.; Timpe, R.C.; Hawthorne, S.B.; Miller, D.J. "Determination of Elemental Sulfur in Coal by Supercritical Fluid Extraction (SFE) and Gas Chromatography with Atomic Emission Detection (GC/AED)," *Fuel* 1992, in press.
2. Louie, P.K.K.; Timpe, R.C.; Hawthorne, S.B.; Miller, D.J. "Determination of Elemental and Organic Sulfur in Coal Using Supercritical Fluid Extraction (SFE) and Pyrolysis/SFE," Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 9-12, 1992.
3. Louie, P.K.K.; Timpe, R.C.; Hawthorne, S.B.; Miller, D.J. "Application of SFE/AED for Sulfur Species Analysis in Coal," Presented at the Second HP AED User Group Meeting, New Orleans, LA, March 9-12, 1992.

6.0 FUTURE WORK

- Perform additional SF water extractions of sulfur from coal.
- Determine effect of additional chemical reactants on SFE of sulfur from coal.
- Determine effect of pretreatment of coal on SFE of sulfur from coal.
- Prepare the final report.

7.0 REFERENCES

1. Allada, R.A. "Solubility Parameters of Supercritical Fluids." *Ind. Eng. Chem. Process Res. Dev.* 1984, 23, 344-348.

2. Rao, V.S.G.; Mukhopadhyay, M. "Effect of Covolume Dependency of the Energy Parameter on the Predictability of SCFE Data Using the Peng-Robinson Equation of State," *J. Supercritical Fluids* 1989, 2, 22-29.
3. Bartle, K.D.; Clifford, A.A.; Shilstone, G.F. "Prediction of Solubilities for Tar Extraction by Supercritical Carbon Dioxide," *J. Supercritical Fluids* 1989, 2, 30-34.
4. Giddings, J.C.; Myers, M.N.; McLaren, L.; Keller, R.A. "High Pressure Gas Chromatography of Nonvolatile Species," *Science* 1968, 162, 67-73.
5. Hawthorne, S.B.; Timpe, R.C.; Miller, D.J. "Sulfur Forms in Coal," Quarterly Technical Progress Report for July - September 1990, Prepared for U.S. Dept. of Energy under Contract No. DE-FC21-86MC10637, Morgantown Energy Technology Center, Morgantown, WV, September 1990.
6. Hawthorne, S.B.; Timpe, R.C.; Louie, P.K.K.; Miller, D.J. "Sulfur Forms in Coal," Semiannual Technical Progress Report for July - December 1991, Prepared for U.S. Dept. of Energy under Contract No. DE-FC21-86MC10637, Morgantown Energy Technology Center, Morgantown, WV, January 1992.
7. Riley, J.T.; Ruba, G.M.; Lee, C.C. "Direct Determination of Total Organic Sulfur in Coal," *Geochemistry of Sulfur in Fossil Fuels*; Orr, W.L.; White, C.M., Eds.; ACS Symposium Series 429, American Chemical Society, Washington, D.C., 1990.
8. Kruse, C.W.; Harvey, R.D.; Rapp, D.M. In *Processing and Utilization of High Sulfur Coals II*; Chugh, T.P.; Caudle, R.D., Eds.; Elsevier: NY, 1987, p 49.
9. Canfield, D.E.; Raiswell, R.; Westrich, J.T.; Reaves, C.M.; Berner, R.A. "The Use of Chromium Reduction in the Analysis of Reduced Inorganic Sulfur in Sediments and Shales," *Chemical Geology* 1986, 54, 149-155.
10. Hackley, K.C.; Buchanan, D.H.; Coombs, K.; Chavan, C.; Kruse, C.W. "Solvent Extraction of Elemental Sulfur from Coal and a Determination of its Source Using Stable Sulfur Isotopes," *Fuel Processing Technology*, 1990, 24, 431-436.

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