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**Resource Characterization and Residuals Remediation,
Task 1.0; Air Quality Assessment and Control, Task 2.0;
Advanced Power Systems, Task 3.0; Advanced Fuel Forms and
Coproducts, Task 4.0**

Topical Report

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**Resource Characterization and Residuals Remediation
Task 1.0**

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EXECUTIVE SUMMARY

This report addresses three subtasks related to the Resource Characterization and Residuals Remediation program: 1) sulfur forms in coal and their thermal transformations, 2) data resource evaluation and integration using GIS (Geographic Information Systems), and 3) supplementary research related to the Rocky Mountain 1 (RM1) UCG (underground coal gasification) test program.

Sulfur Forms in Coal and Their Thermal Transformations

One of the major problems that still plague the coal utilization industry is the lack of cost-effective methods for precombustion sulfur removal from coal. Reliable analytical data on the forms of sulfur in coal are important to the development of an effective sulfur removal method. To assist in developing such a method, numerous attempts have been made to identify and characterize sulfur species in coal using wet chemical methods, Soxhlet extractions, x-ray methods, like x-ray photoelectron spectroscopy (XPS), hydropyrolysis, and temperature-programmed reduction (TPR), to name a few. Each has been moderately successful. The major goal of this project is to isolate sulfur species selectively from the coal matrix for subsequent direct sulfur form identification and quantitation. The technique of choice is supercritical fluid extraction (SFE) combined with gas chromatography-mass spectrometry (GC-MS), stable sulfur isotope MS, and classical wet chemical techniques. Analytical-scale SFE has recently become a popular alternative to solvent extraction, because supercritical fluids have superior mass transfer and diffusivities compared to liquid solvents, involve relatively safe fluids (CO_2), and generate little waste. A rapid, reliable method for extracting and quantitating elemental sulfur from coal at 110°C and 400 atm with 10% methanol in CO_2 was recently developed at the Energy & Environmental Research Center (EERC).

Extraction to remove the remaining sulfur forms, i.e., sulfatic, pyritic, and "organic," was evaluated. Sulfur removal methods were developed using analytical-scale SFE at 110°C and 400 atm and pyrolysis-SFE at 450°C and 400 atm on bituminous coal samples obtained from the Illinois Basin Coal Sample Program (IBCSP) and on Indiana No. 3 coal samples from AMAX. Experiments using pyrolysis were performed to obtain real-time extraction information for a high-severity SFE study. Greater than 80% of the total sulfur was extracted from coal treated with H_3PO_4 (phosphoric acid) with CO_2 at 450°C and 400 atm. Methanol-modified CO_2 extracted 62% of sulfur from coal, whereas 48.5% was extracted from the same coal with pure CO_2 at 450°C and 400 atm. A H_3PO_4 -spiked coal sample also provided the highest total sulfur removal compared to samples spiked with ethanol or acetic acid.

The American Society for Testing and Materials (ASTM) sulfate determination requires extraction of the coal sulfate with gently boiling 4.8 M HCl (hydrochloric acid). However, in following the procedure, as much as 15% of the nonsulfatic sulfur was lost and thus unidentified, making the sulfur mass balance unacceptable. The ASTM method that determines organic sulfur by difference would arbitrarily assign the lost sulfur to the "organic" form. Replacing the HCl with formic acid for sulfate extraction reduced this loss, resulting in acceptable sulfur closure. The better closure reduced uncertainty in any subsequent pyritic and organic sulfur determination from the acid-treated residue. Stable sulfur isotope analysis indicated that HCl extraction was removing some organic sulfur, since the $\delta^{34}\text{S}$ value of sulfate sulfur obtained by HCl was about 2‰ (per mille) lower

than the value obtained with the formic acid method. Extraction with either HCl or formic acid appears to leave the coal matrix relatively intact compared to HNO₃ (nitric acid) extraction.

Data Resource Evaluation and Integration Using GIS

The long-term objective of the second subtask reported here, the Resource Data Evaluation project, is the development of methods that incorporate all of the fundamental aspects of resource characterization, utilization, and reclamation within a single integrated system. GIS (Geographic Information Systems) technologies for data management are being evaluated, demonstrated, and integrated into EERC energy and environmental programs. GIS, which permits map-based data from various sources to be layered as desired, may be best thought of as a method of analysis that supports the decision-making process of an organization.

Test cases using field resource data from the coal-bearing strata of the Fort Union area of northwestern North Dakota and from western Slope County in southwestern North Dakota were used to determine by example how to apply GIS to various coal resource projects ongoing at the EERC. A number of advanced programming techniques were developed as a first step toward full implementation of GIS capabilities.

Supplementary Research Related to the Rocky Mountain 1 UCG Test Program

The concluding activities of the RM1 UCG test program are focused on the evaluation of the extremely large and varied database that was generated prior to, during, and following the test of the two UCG technology variations that were the focus of the program. The two activities addressed here each represent an effort to maximize the utility of a particular portion of that database.

The first activity involves the overburden and groundwater temperature data that were collected on a periodic basis at the RM1 site. Specifically, with the aid of the Cray X/MP supercomputer system at the University of North Dakota, these data are being used as the basis for fine-scale modeling of the test-related hydrothermal regime in and around the RM1 test cavities in the context of the transient conditions that characterized the site during the test and posttest periods. Also being addressed as part of this modeling effort is the issue of the heat sources for this hydrothermal regime. To date, this effort has primarily involved the transformation of an existing PC-based computer code for use on the Cray system, as well as the preliminary testing and refinement of the transformed code.

The second activity is designed to produce an "atlas" of the mineral and amorphous phases identified during the course of the extensive effort to characterize the test-related, thermally altered solid materials from the RM1 site. This atlas is intended as a mechanism for providing ready access to phase-specific information, data, and insights that will be particularly useful to those involved in the design, siting, conduct, and evaluation of future UCG operations. Specifically, individual sections devoted to each of the identified phases will include 1) key identification criteria for the most applicable analytical techniques; 2) information on the occurrence of the phase in the RM1 thermally altered materials, including the form(s) it takes, the frequency of its occurrence, and the

other phases with which it is associated; 3) comments on the origin of the phase at the RM1 site; and 4) a brief summary of the primary implications of the phase in the UCG context. To date, this effort has primarily involved 1) the development of an outline for the atlas and the completion of several phase-specific sections as a means of establishing the atlas contents and format; 2) the review and selection of particularly illustrative characterization data and photomicrographs for inclusion in the atlas; 3) the development of plans to selectively generate required illustrative material that is not presently available; and 4) the completion of preliminary drafts of about 20 additional phase-specific sections.

TASK 1.0 RESOURCE CHARACTERIZATION AND RESIDUAL REMEDIATION

Subtask 1.1 Sulfur Forms in Coal and their Thermal Transformations

INTRODUCTION

There has been no reliable method to identify and quantitate sulfur forms in various coals and coal products (including chars). This ability is necessary to support new engineering approaches for reducing sulfur content in coal products and emissions. Current analytical tests (ASTM D2492, D271) separate coal sulfur into pyritic (calculated from iron measurements), sulfatic, and organic (calculated by difference). Only total sulfur and sulfate (a minor fraction) are based on direct measurements. The pyritic sulfur value is subject to criticism, since it is based on a measure of iron assumed to adhere rigidly to the stoichiometry of mineral pyrite rather than on that of sulfur itself. "Organic" sulfur from the ASTM method is particularly objectionable, since it is a difference value and includes S species which are not organic, such as elemental and sulfidic sulfur, as well as hundreds to thousands of organic compounds including (but not limited to) thiophenes, condensed thiophenes, aryl sulfides, disulfides, mercaptans, thiophenols, and polysulfides.

During the past year in this laboratory, a reliable supercritical fluid extraction (SFE) method for determining the elemental sulfur in coal was developed. With this method, the uncertainty in the measurement of organic sulfur in coal was somewhat reduced. The method was published in *Fuel* (1). In the past year, work also progressed toward refining methods for determining sulfatic sulfur more accurately. Stable sulfur isotope analysis was used to determine selectivity of extraction techniques. Development of a method for extracting pyritic sulfur and for direct organic sulfur analysis as begun.

OBJECTIVES

The investigation was a continuation of promising work begun last year to develop a reliable, convenient analytical method for the direct determination of organic sulfur in coal and chars. The objectives of the second year's investigation were as follows:

1. To investigate and develop the use of supercritical fluid extraction (SFE) and pyrolysis/SFE for the selective extraction of true organic sulfur forms from coal. Also, to identify and quantitate the individual S organics recovered from SFE procedures.
2. To develop and evaluate on-line SFE methods for pyrolysis, extraction, and analysis as needed to achieve mass balance between extracted and collected organic sulfur.
3. To determine the relationship between various inorganic and organic sulfur forms using class-selective extractions and stable sulfur isotope ratio measurements.
4. To evaluate and incorporate other promising sulfur speciation techniques.

ACCOMPLISHMENTS

Experimental

Bituminous coals, IBC-101, IBC-102, IBC-106, and IBC-107 obtained from the Illinois Basin Coal Sample Program (IBCSP), and washed and magnetically cleaned Indiana No. 3 coal sample from AMAX Research and Development Center were used for this investigation. All of the coal samples used in this work were ground under a stream of argon to $-75\ \mu\text{m}$ and stored under argon in plastic containers before use. The proximate analysis of the coals are shown in Table 1.1-1. Work on stable sulfur isotope mass spectrometry in identifying sulfur forms in IBC-101, IBC-102, IBC-106 and IBC-107 continued from the past year. These coals were also extracted to determine quantitative variation in sulfate extraction between ASTM 4.8 M HCl extraction and the 1.0 M HCl extraction used by the stable isotope analysis group in Leeds U.K. The effectiveness of nonhalogenated acids for the extraction of sulfate sulfur was also tested on these coals.

Sample Preparation

Elemental sulfur-free coal (1) was prepared in 5-g quantities using a Suprex Prepmaster pump (Suprex Corp., Pittsburgh, PA, USA) under mild SFE conditions ($\text{CO}_2/10\%$ methanol, 400 atm, 110°C , 100 min) and 10.4-mL Keystone SFE extraction cell (Keystone Scientific, Bellefonte, PA, USA). A 10-cm long crimped stainless steel tube ($1/16$ in. OD $\times$ 0.020 in. ID) was attached at the outlet of the extraction cell to regulate the fluid flow (typically $1.5\ \text{mL}/\text{min}^{-1}$ as pressurized fluid measured at the pump), and the extracted effluent was collected by depressurizing into a sample vial containing 3 mL of toluene (Optima grade, Fisher Scientific, Pittsburgh, PA, USA). The analysis of the extract was performed at regular intervals by gas chromatography with atomic emission detection (GC-AED, Hewlett-Packard Company, Avondale, PA, USA). Since no elemental sulfur was detected from extracts obtained during the final 15 minutes, quantitative removal of the elemental sulfur was assumed.

Sulfate sulfur-free coal was prepared according to ASTM D2492, an HCl extraction procedure (2). Two-gram coal samples were extracted with boiling 4.8 N HCl, washed with water, filtered, and dried in an oven at 100°C for 2 hr. The sample was then stored under argon in plastic containers until used. Similarly, coal samples that were free of elemental and sulfate sulfur were obtained by performing HCl batch extraction on elemental sulfur-free coal samples.

Pyritic and sulfatic sulfur-free coal samples were obtained by performing HNO_3 batch extractions on both raw and elemental sulfur-free coal samples in accordance with ASTM method D2492 (2). Two-gram coal samples were extracted with boiling 2 N HNO_3 , washed with water, filtered, and dried in an oven at 100°C for 2 hr. The sample was then stored under argon in plastic containers until used.

Pyrolysis/SFE

Pyrolysis/SFE experiments were performed on 50-mg coal samples that were mixed with 50 mg of clean sand (sea sand, Fisher Scientific). The presence of the sand prevented the bituminous coal samples from agglomerating on heating, which would prevent maximum fluid-coal contact. Premixed 10% (v/v) methanol in CO_2 (Scott Specialty Gases)

TABLE 1.1-1

Proximate and Total Sulfur Analysis of Coal Samples, wt%					
	IBC-101	IBC-102	IBC-106	IBC-107	Indiana No. 3
Moisture	13.56	14.01	10.49	11.16	4.84
Volatiles, mf*	41.43	39.89	40.27	39.85	41.74
Fixed C, mf	48.35	53.95	51.21	48.78	46.82
Ash, mf	10.24	6.20	8.51	11.37	11.53
Total S	4.31	3.07	3.59	3.44	4.20

* mf = moisture-free.

TABLE 1.1-2

Sulfur Forms Analysis of Coal Samples ^a , wt% mf					
Coal Sample	Elemental ^b	Sulfatic	Pyritic	Organic ^c	Total
IBC-101	0.11	0.67	0.53	3.13	4.44
IBC-102	0.35	1.17	0.61	1.14	3.27
IBC-106	0.20	0.73	0.72	2.03	3.68
IBC-107	0.05	0.37	0.42	2.75	3.59

^a Analysis performed by Minnesota Valley Testing Laboratories, Inc., Bismarck, ND

^b Reference elemental paper (1).

^c Organic sulfur adjusted to account for elemental sulfur.

was used to supply the methanol-modified CO₂ for the 30-min extractions unless other additives were used. Additives, including approximately 200 μ L of 85% phosphoric acid, ethanol, or glacial acetic acid were spiked on the sample and then extracted using pure supercritical CO₂.

The extraction cell was pressurized to 400 atm and held under static conditions while the oven was heated rapidly at about 32°C/min⁻¹ to 450°C (requiring about 13 min). The dynamic extraction was then begun and continued for 30 min at 400 atm and 450°C.

Following extraction, the oven was cooled to ambient temperature before the extraction cell was detached from the extraction line for safety and to prevent any possible loss of material. The entire content of the extraction cell was collected and analyzed for total sulfur in accordance with ASTM guidelines. The extent of sulfur species removal from either untreated or treated coal feeds (expressed in percentage of sulfur removed) was determined by comparing the total sulfur content in the SFE-extracted residues (in mg of sulfur) with that in the untreated raw coal (in mg of sulfur).

To reduce the loss of extremely volatile species, on-line pyrolysis/SFE/GC-MS was used in the extraction and analysis of sulfur from 1-mg coal samples. Pyrolysis/SFE extract was collected cryogenically (-50°C) at the inlet of a DB-5 GC column. Following

the extraction, the condensed extract was desorbed onto the GC column and analyzed with the MS.

Results and Discussion

This project involves the development of a series of procedures with which sulfur forms can be measured directly, quickly, accurately, and economically. The strategy involves removal of forms by sequential extractions and measurement of the sulfur. As the method for each form becomes available, the procedure and experimental results of the developmental work will be published in refereed journals. Two publications relating the work completed during this reporting period are referenced (1, 3).

Elemental sulfur was extracted from four coals, IBC-101, IBC-102, IBC-106, and IBC-107, with supercritical $\text{CO}_2/10\% \text{CH}_3\text{OH}$ at 110°C and 400 atmospheres. The residues were then analyzed in duplicate for SO_4^{2-} by the ASTM sulfate method described in D2492. This procedure, in which Ba^{++} is used to precipitate the SO_4^{2-} after it has been extracted from the coal with hot HCl , is a relatively simple, straightforward gravimetric method to directly determine that form of sulfur. To test this method and its reproducibility and to compare it with the method used by Dr. Simon Bottrell of the University of Leeds, UK, (Methods 1 and 2 on Table 1.1-3) for obtaining sulfur forms for stable sulfur isotope analysis in his laboratory, the coals were extracted in duplicate under air and under N_2 at two temperatures. Table 1.1-3 shows the results obtained with these extractions. Reproducibility of results for all duplicates was excellent. No real difference in SO_4^{2-} was observed between the results of an extraction done at a given acid strength and at a given temperature under air compared with that done under N_2 . Slightly more sulfate was extracted from the IBC-101 and the IBC-107 with the 4.8 M (ASTM) HCl than with the 1 M (Bottrell) HCl . Total sulfur analyses of the extracted residues gave results similar to those just described for the sulfate analyses of the corresponding extract. However, in calculating sulfur mass balance, there appeared to be only slight loss of sulfur in IBC-101, but a much greater loss of sulfur in the IBC-107, indicating that the HCl extraction is probably removing sulfur species in addition to SO_4^{2-} , suggesting that the HCl extraction method is coal-specific. This has the effect of revealing a second source of error in the ASTM sulfur forms analysis (the first being the lack of determination of elemental sulfur, thus lumping it in with the "organic" sulfur value which is calculated by difference).

To address the problem of poor mass balance in some coals (represented here by IBC-107) other acids were used to extract the sulfate from the four elemental sulfur-free coals. The method was identical to that used in the HCl extractions, except that the phosphoric and formic acids were substituted for the HCl . As expected, the phosphate coprecipitated with the sulfate, giving a barium residue 8 times that expected for the pure barium sulfate. The formic acid extract, however, yielded sulfate results identical to those of the HCl extracts, but, even more importantly, gave sulfur mass balance results much better than those of HCl -extracted samples. The mass balance results in Tables 1.1-4 and 1.1-5 can be compared to see the improvement.

While sulfate sulfur yields from coal samples IBC-101, -102, -106 and -107 obtained by extraction with formic acid appeared to be consistent with the yields obtained using the ASTM HCl method and, in addition, yielded superior sulfur mass balance values, determination of the sulfate sulfur by an independent spectroscopic method (such as stable

TABLE 1.1-3

Sulfur in Coal Residue Samples and Sulfate Extract					
	SFE	HCl		Sulfatic Sulfur	Sulfur
	Extracted	Extracted	Sulfate	in Coal, wt%	Recovery, %
	Sulfur, mg				
Method 1 (1 M HCl, N ₂)					
IBC-101	74.35	53.76	11.77	0.57	88.14
IBC-101	72.21	55.76	12.02	0.60	93.87
IBC-107	69.31	52.10	6.27	0.31	84.22
IBC-107	67.60	49.15	6.12	0.31	81.76
Method 2 (1 M HCl, N ₂ , heated to 95°C)					
IBC-101	72.48	53.31	13.32	0.67	91.93
IBC-101	72.68	55.60	12.48	0.62	93.67
IBC-107	67.78	49.96	6.65	0.33	83.52
IBC-107	67.78	50.71	6.29	0.31	84.10
Method 3 (4.8 M HCl, air, heated to 95°C)					
IBC-101	72.51	54.83	14.33	0.72	95.38
IBC-101	72.46	53.00	13.57	0.68	91.87
IBC-107	67.56	49.05	7.21	0.36	83.27
IBC-107	67.60	49.55	6.94	0.35	83.57
Method 4 (4.8 M HCl, air, boiled at 110°C)					
IBC-101	72.68	57.59	13.59	0.68	97.94
IBC-101	72.47	55.60	13.10	0.65	94.80
IBC-102	51.24	25.37	20.85	1.04	90.20
IBC-102	51.07	27.17	20.52	1.02	93.38
IBC-106	62.41	42.72	15.83	0.79	93.82
IBC-106	62.14	40.19	16.11	0.80	90.60
IBC-107	67.74	52.84	6.84	0.34	88.10
IBC-107	67.84	51.62	6.89	0.34	86.24
Method 5 (4.8 M HCl, N ₂ , heated to 95°C)					
IBC-101	72.51	56.41	12.97	0.65	95.68
IBC-101	72.72	54.81	12.64	0.63	92.75
IBC-107	67.74	49.42	7.15	0.36	83.51
IBC-107	67.67	49.72	6.80	0.34	83.52

TABLE 1.1-4

Percentage of Sulfur Recovery After Formic Acid Extraction				
	Sulfur, %		Sulfate, wt%	
	Formic Acid- Extracted Residue	Sulfate Extracted- Residue	Sulfur in Coal	Percent Recovery
IBC-101	79.54 ± 2.37	15.16 ± 1.93	0.61 ± 0.08	94.7 ± 4.30
IBC-102	56.05 ± 4.96	39.23 ± 1.31	0.93 ± 0.03	95.28 ± 6.27
IBC-106	76.37 ± 0.71	23.96 ± 3.54	0.64 ± 0.09	100.33 ± 4.25
IBC-107	85.10 ± 4.87	10.39 ± 0.39	0.34 ± 0.01	95.49 ± 5.26

TABLE 1.1-5

ASTM Sulfur Forms Analyses of Coal Samples, moisture-free basis

	ASTM S				
	IBC-101	IBC-102	IBC-106	IBC-107	Indiana No.3
Pyritic	1.09	1.66	1.50	0.51	0.49
Sulfatic	0.07	0.16	0.11	0.29	0.83
Organic	3.36	1.58	2.29	2.76	3.09
Total	4.53	3.41	3.90	3.55	4.41

sulfur isotope mass spectrometry) was needed to confirm the sulfate results. Stable sulfur isotope mass spectroscopy based on the natural isotopic ratios ($\delta^{34}\text{S}:\delta^{32}\text{S}$) of sulfur has been successfully applied in tracking sulfur and differentiating sulfur forms in coals.

This method is particularly valuable in analyzing ^{34}S -enriched samples such as IBC-107, and it is for this reason that much of our stable sulfur isotope work and that of Hackley, et al, [4] has focused on that coal before being extended to the other coals. A comparison of sulfate sulfur obtained with formic acid extraction and the standard ASTM HCl extraction method was obtained from the corresponding $\delta^{34}\text{S}/\delta^{32}\text{S}$ values. Any significant amount of pyritic and organic sulfur coextracted with sulfate sulfur and subsequently counted as sulfate sulfur could be observed by the stable sulfur isotope results. To this end, sulfate sulfur samples in the form of barium sulfate, obtained under extraction conditions different from those under which coal samples IBC-101, -102, -106, and -107, were analyzed by stable sulfur mass spectroscopy. The $\delta^{34}\text{S}$ values obtained are given in Table 1.1-6. The corresponding weight percent sulfate sulfur in coal and percent sulfur recovery values are also given in Table 1.1-6 for comparison. Essentially the same $\delta^{34}\text{S}$ values were obtained for sulfate sulfur extracted from IBC-101, -102, -106 and -107 by using Method 1 (+1.0, +5.1, +5.8, and +16.0‰) and Method 6 (+1.5, +7.7, +7.7, and +18.2‰), which indicated that formic acid extracted the same sulfate fraction as the standard ASTM HCl method.

Similar $\delta^{34}\text{S}$ values on sulfate sulfur were obtained under a broad range of HCl extraction conditions (Methods 2, 3, 4, and 5) from IBC-101 and IBC-107 supporting the previous findings that under all of the conditions tested, HCl extracted the same sulfate sulfur fraction. Since the $\delta^{34}\text{S}$ values of sulfatic, pyritic, and organic sulfur are +13.2, +23.4, and +1.8, respectively, for coal sample IBC-107, if a significant portion of the organic or pyritic sulfur were coextracted with either HCl or formic acid, the sulfate sulfur $\delta^{34}\text{S}$ values would have a less positive isotope ratio in the presence of organic sulfur (e.g., organic $\delta^{34}\text{S}$ value +1.8‰ [4]) or a more positive isotope ratio in the case of pyritic sulfur contamination (e.g., pyritic $\delta^{34}\text{S}$ value +23.4‰).

The small difference between our $\delta^{34}\text{S}$ sulfate numbers (+16.0 and +18.2‰) obtained with ASTM HCl and formic acid extraction and the $\delta^{34}\text{S}$ sulfate number reported by Hackley (+13.2‰) probably resulted from the use of a more oxidized coal sample in the present investigation. The sulfate sulfur in coal obtained in the present study was 0.34 wt% compared with 0.26 wt% reported by Hackley et al. [4]. In addition, the sulfate

TABLE 1.1-6

Stable Sulfur Isotope Data of Sulfate Sulfur Obtained under
Different Extraction Conditions

Sample ID	Treatment/Extraction Method	$\delta^{34}\text{S}_{\text{CDT}}$	Sulfatic Sulfur in Coal, wt%	Sulfur Recovery, %
IBC-101	Method 1 (4.8 M HCl, air, gentle boil)	+1.0	0.67	96.37
IBC-102	Method 1 (4.8 M HCl, air, gentle boil)	+5.1	1.03	91.79
IBC-106	Method 1 (4.8 M HCl, air, gentle boil)	+5.8	0.80	92.21
IBC-107	Method 1 (4.8 M HCl, air, gentle boil)	+16.0	0.34	87.17
IBC-101	Method 2 (1 M HCl, N ₂)	+1.6	0.59	91.01
IBC-101	Method 3 (1 M HCl, N ₂ , heated to 95°C)	+1.3	0.65	92.8
IBC-101	Method 4 (4.8 M HCl, N ₂ , heated to 95°C)	+1.2	0.64	94.22
IBC-101	Method 5 (4.8 M HCl, air, heated to 95°C)	+0.3	0.70	93.63
IBC-107	Method 2 (1 M HCl, N ₂)	+16.8	0.31	82.99
IBC-107	Method 3 (1 M HCl, N ₂ , heated to 95°C)	+19.3	0.32	83.81
IBC-107	Method 4 (4.8 M HCl, N ₂ , heated to 95°C)	+17.3	0.35	83.42
IBC-107	Method 5 (4.8 M HCl, air, heated to 95°C)	+17.2	0.36	83.52
IBC-101	Method 6 (4.8 M formic acid, air, gentle boil)	+1.5	0.61	94.7
IBC-102	Method 6 (4.8 M formic acid, air, gentle boil)	+7.3	0.93	95.28
IBC-106	Method 6 (4.8 M formic acid, air, gentle boil)	+7.7	0.64	100.30
IBC-107	Method 6 (4.8 M formic acid, air, gentle boil)	+18.2	0.34	95.49

sulfur yields from the Illinois coals obtained by using either HCl or formic acid are nearly identical (based on barium sulfate gravimetric method and stable sulfur isotope analysis) and a better sulfur mass balance was obtained with formic acid extraction. Therefore the lack of sulfur mass balance (e.g., IBC-107) cannot be attributed to the loss of sulfate, but to an as-yet unidentified coal-dependent HCl acid reaction that results in a sulfur species that has not been collected.

Stable sulfur isotope analysis of the extracts of IBC-107 obtained by SFE (elemental S), HNO₃ extraction (pyritic sulfur, or, in the case of raw coal, pyritic and sulfatic coal) and Canfield extraction (pyritic sulfur) [5] were carried out and the results shown in Table 1.1-7. (Sulfatic sulfur isotope values are given in Table 1.1-6.) The isotope ratio of the pyritic sulfur is said to be "heavy" since it has a relatively large amount of ^{34}S (+26.4‰). Conversely, the "organic" sulfur ratio is said to be "light" because of its relatively small amount of ^{34}S (+1.5‰). Elemental sulfur has an isotope ratio of +13.4‰ that is related to a combination of pyritic and "organic" sulfur, indicating that an interconversion pathway to or from elemental sulfur would include both forms. Similarly, the nitric acid extract of the coal has an isotope ratio of +12.1‰ indicating that the nitric acid has extracted not only the intended pyritic sulfur but also some of the "organic" form. The residue from this extraction is uniquely "organic," as indicated by the +1.6‰ value. The sulfur isotope ratio for the sulfatic sulfur (about +18‰) is most similar to that of pyritic sulfur, indicating that interconversion between those two forms is likely.

TABLE 1.1-7

Sulfur Isotopic Composition of Fractions Obtained from IBC-107

Sample	Preparation	$\delta^{34}\text{S}^\circ/\infty_{\text{CDT}}^1$	Error, %
1	Parr bomb oxidation of total coal	+6.5	± 0.2
2	Parr bomb oxidation of elemental S in SF extract collected in toluene	+13.4	± 0.2
3x	Pyrite sulfur extracted from PL-3 by acidic chromous chloride (Canfield method)	+26.4	± 0.4
3r	Organic S (residue from Canfield extraction) by Parr bomb oxidation	+1.6	± 0.2
4	Inorganic S in Riley ² extract of PL-3	+12.1	± 0.2
5	Organic S (residue from Riley extraction) by Parr bomb oxidation	+1.5	± 0.2

¹ CDT = Canyon Diablo Troilite.² Boiling 2N HNO₃ for 30 minutes.

Traditional sulfur forms analysis yielded the results shown in Table 1.1-5. IBC-101, IBC-106, IBC-107 and the Indiana 3 coals were high in "organic" sulfur. As a result, substantial sulfur removal from the sample, i.e., more than 35%, implies a reduction in that form. Elemental sulfur free IBC-101 and Indiana 3 were extracted in triplicate under static conditions with the fluids shown in Table 1.1-8 followed by dynamic extraction with supercritical CO₂ at 450°C. The results shown in Table 1.1-8 indicate that a great deal more than 35% sulfur reduction occurs in all cases. The H₃PO₄ spike followed by pyrolysis/SFE removes about 80% of the sulfur, whereas less severe additives such as ethanol, acetic acid, and methanol followed by pyrolysis/SFE remove about 40% to 60%.

The results shown in Table 1.1-9 using the raw, sulfate-free, and sulfate- and pyrite-free IBC-101 and Indiana 3 coals demonstrate that both pyrolysis/SFE conditions with and without H₃PO₄ remove a substantial portion of the true organic sulfur. Assuming that the HCl extraction quantitatively removes sulfate and that the HNO₃ extraction quantitatively removes sulfate and pyrite, the percentage of organic sulfur removed by CO₂/10% methanol only or by the addition of phosphoric acid followed by pyrolysis/SFE can be estimated. For example, if 70% of the sulfur in IBC-101 is organic and if CO₂/10% methanol combined with HNO₃ extraction removed 78% of the total sulfur (Table 1.1-4), then the minimum fraction of true organic sulfur extracted by pyrolysis/SFE with CO₂/10% methanol would be 73% (78% total sulfur removed minus 27% inorganic removed by HNO₃ equals 51% of total sulfur extracted by SFE, which is equivalent to 73% of the organic sulfur removed by SFE). Similarly, pyrolysis/SFE with CO₂/methanol extracts a minimum of 70% of the true organic sulfur from the Illinois No. 3 coal.

The results shown in Table 1.1-9 also demonstrate that the addition of H₃PO₄ causes the extraction of both sulfate and pyrite as well as a substantial portion of the organic

TABLE 1.1-8

Percentage of Sulfur Removal from Elemental Sulfur-Free IBC-101 and Indiana No. 3
with Various Supercritical Fluids

Supercritical Fluids/Reagent	Percentage of Total Sulfur Removed ¹	
	IBC-101	Indiana No. 3
CO ₂	49 ± 1	-- ²
CO ₂ /Methanol	62 ± 3	60 ± 7
CO ₂ /Acetic Acid	43 ± 2	--
CO ₂ /Ethanol	48 ± 1	--
CO ₂ /Phosphoric Acid	82 ± 3	78 ± 9

¹ Standard deviations are based on triplicate 30-min extraction.

² Not determined.

TABLE 1.1-9

Pyrolysis/SFE Sulfur Removal from IBC-101 and Indiana No. 3
Using Supercritical CO₂/10% Methanol and CO₂/Phosphoric Acid

Coal Samples	Sulfur Removal on Total Sulfur Basis ¹			
	CO ₂ /MeOH		CO ₂ /Phosphoric Acid	
	IBC-101	Indiana No. 3	IBC-101	Indiana No. 3
Raw	62 ± 3	60 ± 7	82 ± 3	78 ± 9
Sulfate-Free	70 ± 1	72 ± 1	83 ± 13	85 ± 23
S ₈ - and SO ₄ -Free	68 ± 1	68 ± 2	81 ± 12	84 ± 7
SO ₄ - and FeS ₂ -Free	78 ± 1	76 ± 3	78 ± 13	81 ± 12
S ₈ -, SO ₄ -, FeS ₂ -free	81 ± 2	72 ± 4	80 ± 11	74 ± 10

¹ Standard deviations are based on triplicate 30 min extraction.

sulfur. Again, assuming that the HNO₃ quantitatively extracts the sulfate and pyrite, the minimum fraction of organic sulfur extracted by pyrolysis/SFE with the addition of phosphoric acid would be 69% and 73% for IBC-101 and Illinois No. 3, respectively.

Extractions at elevated temperatures and under pressure may have an effect on coal matrices. Coal structure may be altered during SFE or hot acid extractions, potentially affecting the sulfate sulfur determination. To determine the extent of these effects, thermogravimetric analysis (TGA) were performed on the untreated (raw coal), SFE-treated (elemental sulfur-free), SFE- and HCl- treated (elemental and sulfate sulfur-free),

and SFE- and formic-acid treated (elemental and sulfate sulfur-free) IBC-101 coal samples. The results are shown in Table 1.1-9. The moisture, volatile matter, combustible residue (fixed carbon) and noncombustible residue (ash) values determined are given in Table 1.1-10. Apart from a small reduction in the residue caused by mineral dissolution in the acid-treated samples (both HCl and formic), there is no apparent difference in the amounts of thermally labile components of the SFE-treated, SFE-HCl treated and SFE-formic acid-treated samples, indicating minimum structural changes of the raw coal as it undergoes these extractions. However, when the coal is extracted with nitric acid to remove pyritic sulfur according to ASTM D2492, the coal matrix undergoes severe changes, as shown in Table 1.1-10.

Conclusions

1. An extraction method based on pyrolysis/SFE conditions for extracting sulfur species from coal samples showed promise, with 82% and 78% of sulfur, respectively, removed from H_3PO_4 -treated IBC-101 and Indiana No. 3 treated with supercritical CO_2 at $450^\circ C$ and 400 atm as opposed to 62% and 60% respectively, using 10% methanol in CO_2 under the same conditions.
2. Since pre-extraction with HNO_3 to remove sulfatic and pyritic sulfur was required to obtain a total sulfur removal of about 80% by SFE, it appears that extraction with CO_2 /10% methanol at $450^\circ C$ and 400 atm selectively removes organic sulfur.
3. Formic acid extraction of sulfatic sulfur results in better sulfur closure than HCl extraction, indicating the HCl may be removing additional sulfur lost by some as yet unidentified mechanism. The better sulfur closure with the formic acid method may reduce uncertainty in any subsequent pyritic and organic sulfur determination from the acid-treated residue.

TABLE 1.1-10

Proximate Analysis of Untreated, SFE-, HCl- and Formic Acid-Treated IBC-101 Samples

Coal Sample	Moisture, wt%	Volatile Matter, wt%	Fixed Carbon, wt%	Residue (ash), wt%
Untreated	9.0	35.8	44.6	10.5
S_8 -Free	5.0	36.5	47.6	11.0
S_8 - and Sulfate-Free ¹ (HCl-extracted)	4.3	36.7	51.2	7.9
S_8 - and Sulfate-Free (formic acid-extracted)	5.4	37.5	49.8	7.3
S_8 -, SO_4 -, Pyrite-Free ² (Nitric acid-extracted)	6.1	75.5	15.7	2.8

¹ Performed using Method 5 (4.8 M HCl, air, gentle boil).

² Performed using Method 6 (4.8 M HCl, air, gentle boil).

4. Stable sulfur isotope analysis indicates that HCl extraction may be removing some "organic" sulfur, since the $\delta^{34}\text{S}$ value of sulfate sulfur obtained with HCl is typically 2‰ lower than that obtained with the formic acid method.
5. Extraction with either HCl or formic acid appears to leave the coal matrix relatively intact compared to HNO_3 extraction.
6. ASTM sulfate sulfur extraction is coal-specific, whereas formic acid extraction is independent of the coals used in this study.

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TASK 1.0 RESOURCE CHARACTERIZATION AND RESIDUAL REMEDIATION

Subtask 1.3 Data Resource Evaluation

INTRODUCTION

The long-term objective of the Resource Data Evaluation project is the development of methods that incorporate all of the fundamental aspects of resource characterization, utilization, and reclamation within a single integrated system. This project will approach its objective through the use of Geographic Information Systems (GIS) technologies as a data management tool. The project will evaluate and select GIS programming and provide initial demonstration of its utility in ongoing projects, to be followed by implementation of the system within the energy and environmental research programs at the EERC.

Advances in computer hardware and software technology are reshaping the approach to data acquisition, management, and analysis. Significantly, data sharing, or data availability, has become an important outcome of the increase in agencies and institutions striving for an integrated approach to resolving the myriad of complex global concerns. At the vanguard of the integrative technologies is the approach known as GIS. This software technology permits the input, manipulation, analysis, and display of geographically referenced data. As such, GIS represents a set of tools to perform a variety of functions directed toward integrating both map information and associated attribute data. The portrayal and analysis of such information can occur at many levels of specificity. Many traditional map-oriented endeavors, from geology to city planning, are well suited for use in GIS programming. The strength of GIS, however, is in its capability to integrate and portray the relationship between data typically left unassociated because of the lack of a means to bring different types of information into one format and method of analysis (say, for example, the cost relationship between geology and urban sewer systems). The final display of information for the user is no longer the major and costly task of a project, freeing the user to explore alternative approaches to understand the relationship between data of different types. Investigation, not compilation and display, thus becomes (or remains) the central research issue. The ongoing development of GIS software is analogous (on a much higher plane of complexity) to the advent of sophisticated word processing or spreadsheet programming. The clerical responsibility is no longer just the production of error-free typed reports, but the manipulation of information to produce publication-quality documents.

GIS may be best thought of as a method of analysis that supports the decision-making process of an organization. The question, What if? is likely to be explored to great advantage employing GIS technology. Interpreting the relationships between various social concerns, such as topography and land use, coal quality and utilization, or air emissions and pollution, are important to effective resource management, but have not traditionally been easily related as single issues or as a complex of problems. The various types of analytical procedures available to the GIS user would be difficult to employ in traditional mapmaking. The conversion of qualitative observations to coded digital information makes data generally available for any number of applications as each data type is treated as a separate layer within GIS programming. The clear advantage of GIS technology is the ability to edit (i.e., revise or add) information in each layer

independently and to relate these layers easily; to produce, in a relatively straightforward manner, a new generation of maps specific to current needs and applications. Existing attribute data can be uploaded to be used in GIS applications. Derived data and geographic locations can be downloaded for use in other graphical, analytical, data management, or word processing programs.

OBJECTIVES

The Resource Data Evaluation initiative consists basically of two component projects representing a single objective, which is to develop an understanding of the analysis capabilities across the spectrum of program areas at the EERC to support data management needs as part of the decision-making process. These program areas include energy and environmental policy and planning, mine planning and reclamation, energy resource occurrence, groundwater resource occurrence, and waste management studies.

In Project 1, Resource Data Integration, research is directed toward the development of an approach to fully integrate a geographically based resource management system to interpret the complex relationships between capability, utilization, and reclamation. The integration of resource data across the large number of energy and environmental concerns requires specialized programming and hardware specific to the information-intensive applications of multilayered attribute data associated with GIS. Commercially available geographical information system software will be utilized with advanced computing systems as the data management system to analyze these relationships. Research will focus on the methodology and system requirements to undertake a sequence of pilot projects.

In Project 2, Resource Data Correlation, research is undertaken to apply GIS technologies by example to determine programming and hardware requirements to utilize a variety of data types. Examples include research areas in the Paleocene age coal-bearing strata of the Williston Basin in North Dakota and adjacent areas in Montana. The objective of this project is to utilize existing EERC databases to integrate coal-related information with geologic information for the specific purpose of summarizing the status of coal bed recognition and correlation in the Williston Basin. Tasks will be directed toward the publication of outcrop area and regional syntheses of Paleocene stratigraphic units for the purpose of a comprehensive nomenclature guide for the Williston Basin portion of the Fort Union lignite area. This information will provide a tool specifically designed for earth resource evaluation and characterization, but will also have applications for groundwater and environmental concerns by providing the means of defining bed and other lithosome correlations in specific areas.

ACCOMPLISHMENTS

The proposed research included a number of activities that were thought to represent a comprehensive approach to fully develop GIS capabilities at the EERC. Interest in using a GIS technology strategy for problem solving and data management has, however, mushroomed between the time the research was proposed and work commenced. The value of a GIS approach does not appear to need to be argued. Researcher interest is in how GIS can be applied to a researcher's data and what needs to be done for the system to become operational. How to facilitate becoming functional in GIS is and will remain the major obstacle to GIS purchases. Major concerns include

potential acquisition of costly software and hardware, training of current or additional staff, getting current data into a GIS mode, and the expense of maintaining the system. As the personal computer has taken the place of mainframes, minis, and micros for many computing needs, will the intensive number crunching associated with GIS programming require more powerful machines and knowledge of different operating systems?

The Resource Data Evaluation project undertook test cases to determine by example how to apply GIS to various coal resource projects ongoing at the EERC. By way of examples, test cases are presented here and will involve the basics of GIS illustrated in Figure 1.3-1. The test cases include the coal-bearing strata of the Fort Union area in northwestern North Dakota and of western Slope County in southwestern North Dakota (Figure 1.3-2). The Fort Union Corridor test case utilized Version 2 of Atlas GIS™ by Strategic Mapping, Inc., to determine at least the initial utility of a PC-based GIS program. Atlas GIS™ was run without difficulty on a 486 Gateway 2000 (4DX2-66V) computer with 3 MB of RAM and compressed drives. Output was directed to a Hewlett-Packard LaserJet III with 3 MB of memory (see figures for examples of illustration capabilities), as well as to other programming (discussed below). The point locations, representing about 400 surface and subsurface geologic observations (Figure 1.3-3), were digitized using a 24- × 36-inch GTCO Corporation Digi-Pad® type 5A with a 16-button cursor and 0.001-in. resolution. A discussion of enhanced programming and database management methods to facilitate GIS capabilities will follow.

The Fort Union Corridor of the Missouri River, North Dakota–Montana (Figures 1.3-2 and 1.3-3) is a project area that includes the surface and subsurface stratigraphic records for northern McKenzie and southern Williams Counties, North Dakota, and northern Richland and southern Roosevelt Counties, Montana. The Fort Union Corridor, as defined by the study, extends from about New Town, North Dakota, to Culbertson, Montana. This area effectively includes the type area of the Fort Union Group, representing the Fort Union coal region, and includes the coal-bearing strata of the Paleocene age Bullion Creek (= Tongue River) and Sentinel Butte Formations. Previous research in the area computerized the location of numerous geologic observations into databases designed and maintained in Q&A® by Symantec Corporation. All of these observations had previously been plotted, as specifically as possible, on 1:24,000-scale U.S. Geological Survey (USGS) topographic quadrangles.

A smaller field study area was selected to deal specifically with the correlation of coal beds and formational contacts. The area of the Nesson Anticline (Figure 1.3-2) was chosen because of the known difficulty of correlating significant coal beds in this area and the attendant lack of consistency on placing the Bullion Creek–Sentinel Butte formational contact (Hartman and others, 1993). The Nesson Anticline was first recognized and delimited by Collier (1918) who produced a structure contour map of the Williston lignite bed. The proposed research attempted to resolve the problems of correlation across the Nesson Anticline utilizing Atlas GIS™ and additional field observations.

As noted above, the management of map-based information in GIS programming treats discrete information types as distinct layers (files) that can be layered as desired. Figures 1.3-4 through 1.3-9 represent a succession of layers derived through the course of the test case of the Nesson Anticline. The cadastral map for this project was digitized from the USGS quadrangles covering the area (Figure 1.3-4). Township and range digital map (DLG) files for these quadrangles could have been purchased either

Figure 1.3-1. GIS computer programming incorporates a variety of data types from a variety of sources that permit a broad-spectrum approach to resource characterization and management.

Figure 1.3-2. Resource Data Evaluation study areas in western North Dakota and eastern Montana include 1) the Fort Union Corridor, 2) the Nesson Anticline (subset), and 3) the Little Missouri River-Greater Slope County (base map produced by GIS programming).

from the U.S. Geological Survey or from a secondary vendor, such as the North Dakota Geological Survey. Added map information, including political (county) boundaries (Figure 1.3-4), roads (Figure 1.3-5), and hydrologic features (Figure 1.3-6) were obtained and derived from U.S. Census Bureau TIGER files available on CD-ROM. Political boundaries of various types are also frequently available as part of software packages, but may vary in quality. The amount of transportation and surface drainage information in TIGER files is enormous. Figure 1.3-5 illustrates all of the digitized roadways, which, except for State Highway 1804, are all graveled. By compositing desired line segments, most of which are only a few tenths of a kilometer in length, the roadways of interest can be selected and illustrated (Figure 1.3-4b). Similarly, there are only a few important tributaries of the Missouri River (here as Lake Sakakawea), which were selected (Figure 1.3-6b) from the tremendous detail provided by the TIGER files (Figure 1.3-6a).

The previously digitized geologic observations represent their own layer (Figure 1.3-7b). They are illustrated here as pluses (on circles) and circles, representing subsurface and surface geologic sections. To provide chronostratigraphic control to the strata of the Nesson Anticline, fossil localities were also digitized from 1:24,000-scale USGS maps to illustrate their geographic distribution (Figure 1.3-7a). Again, this information is represented as a separate layer with its own associated attribute information. For both geologic and paleontologic observations, once the location of the locality was digitized and associated with the unique number representing the occurrence

Figure 1.3-3. Dots represent coal-related geologic observations (M-numbers) along the Missouri River in portions of five counties centered on Fort Union, which represents the namesake of the Fort Union Group and the Fort Union lignite regions. The cadastral system, political boundaries, transportation, hydrology, and geologic observations are layers in a GIS file (see text) (modified from Hartman, 1992b).

(a)

(b)

Figure 1.3-4. In the cadastral system, legal location (township and range) digital data may be purchased or digitized (a). Political boundaries (county) derived from TIGER information are shown for the area of the Nesson Anticline (b).

(a)

(b)

Figure 1.3-5. All transportation TIGER information available for roads is shown for the area of the Nesson Anticline (a). Another data layer is available to display major transportation routes (b) (see Figure 1.3-10).

(a)

(b)

Figure 1.3-6. All subsurface drainage TIGER information available is shown for the area of the Nesson Anticline (a). Major tributaries of the Missouri River (Lake Sakakawea) can be chosen for display (b) (see Figure 1.3-10).

(a)

(b)

Figure 1.3-7. Digitized fossil localities are displayed in the area of the Nesson Anticline (a). Paleontologic data provide the only effective means of providing chronostratigraphic control for strata in the study area. Digitized surface and subsurface geologic observations consisting of measured and geophysical sections and spot coal identifications and thicknesses in the area of the Nesson Anticline can be displayed (b) (see Figure 1.3-10).

(M-numbers and L-numbers, respectively), attribute information was uploaded from databases maintained in Q&A® (by Symantec Corporation), through a dBASE® (Borland International, Inc.) export utility filter in Q&A®. Likewise, longitude derived from Atlas GIS™ were downloaded into EERC databases.

Previous surficial geologic studies in the area of the Nesson Anticline disagreed as to the placement of the Bullion Creek–Sentinel Butte formational contact (Nevin, 1946; Royse, 1967a,b; Spencer, 1978a,b; Spencer, 1981; Clayton and others, 1980a; Carlson, 1985). Although the relative placement of the contact was known to be different among these workers, the criteria, both literally and as portrayed on maps and in sections, needed to be determined. Where geologic maps were produced (as with Royse, Spencer, Clayton, and Carlson), their map data were digitized into Atlas GIS™. An example of the transfer of geologic map units from the North Dakota State Geologic Map (Clayton and others, 1980a) is presented in Figure 1.3-8a. The light and dark stippled units represent the Bullion Creek and Sentinel Butte Formations, respectively. Other geologic maps were digitized and layered for comparison. Of interest and importance, all of the maps, representing map scales of 1:100,000, 1:250,000, and 1:500,000, were originally produced with such care as to permit very precise registration to the cadastral base map and TIGER data file. From a sequence of overlays, the approximate relative stratigraphic position of the respective Bullion Creek–Sentinel Butte formational contact could be derived at certain control points.

The correlation of the Williston lignite bed, as well as other coal beds, was treated by earlier workers, but without consensus as to its identification on the east flank of the Nesson Anticline and in the badland breaks on the south side of the Missouri River. To understand and reinterpret previous records of the Williston lignite bed, the structure contour maps produced by Collier (1918) and Spencer (1978a, 1981) were digitized (Figures 1.3-8b and 1.3-9a). The map produced by Collier (Figure 1.3-8b) was generalized on a few observations on the north side of the Missouri River on the west flank of the Nesson Anticline. Coal bed observations recorded on the south side of the river are for other coal beds. The placement of the Williston lignite bed by Collier (1918) was based on an extrapolation of the relative stratigraphic thickness between these other beds and the Williston, which at best were known from only a few observations. The correlation of the Williston lignite bed by Spencer (1978a, 1981) is represented in Figure 1.3-9a and shows a different structural configuration for the crest of the Nesson Anticline on either side of the Missouri River. The Williston lignite bed is believed to be partly inaccurately identified on the south side of the river.

A revised structure contour interpretation of the relative elevation of the Williston lignite bed is presented in Figure 1.3-9b. This map was constructed from a reevaluation of all of the previously measured surface and subsurface geologic sections in the area of the Nesson Anticline and to the west towards Williston, in the area of its reference section. Additional sections were measured on both sides of the Missouri River by Hartman, Peck, and Kihm, of Minot State University, to serve as controls. Using all available data, the form of the Nesson Anticline is clearly illustrated in Figure 1.3-9b, with the west flank forming a more gentle dip slope than the east (downriver). This diagram was constructed by contouring the elevations of the base of the Williston lignite bed. Such a contour map cannot be made directly in Atlas GIS™, which indicates an important limitation in its analysis capabilities. The elevation and geographic location data were exported to and contoured in Version 4 of SURFER® by Golden Software, Inc.

(a)

(b)

EERC No. JH09110 CDR

Figure 1.3-8.

A digitized portion of the North Dakota State Geologic Map produced by Clayton and others (1977) is shown (a). Light and dark stippled areas represent the Bullion Creek and Sentinel Butte Formations of the Fort Union Group. Structure Contour 1 displays a digitized representation of the structure contour map of the Williston Lignite bed and utilized observations on various lignite beds produced by Collier (1918, pl. XXVI), who first described and named the Nesson Anticline (b).

(a)

(b)

EERC No. JH09111 CDR

Figure 1.3-9.

Structure Contour 2 is a digitized representation produced by Spencer (1978a, 1981), of the Williston lignite bed on the Nesson Anticline (a). Structure Contour 3 is a map of the base of the Williston lignite bed produced by Resource Data Evaluation studies utilizing reevaluated and newly taken observations (b) (see Figure 1.3-10).

Once contoured, the map image was saved as a DXF file and imported into Version 3 of CorelDRAW® by Corel Corporation. The layered cadastral (Figure 1.3-4a), political boundaries (Figure 1.3-4b), selected roads (Figure 1.3-5b), selected hydrology (Figure 1.3-6b), and observations on the Williston lignite bed (derived from Figure 1.3-7b) were exported from Atlas GIS™ and imported into CorelDRAW® as a CGM file type. The control and registration of the Atlas GIS™ derived data in CorelDRAW® is precise, and each of the GIS layers can be treated independently. The contour map produced in SURFER® is added as a layer and registered. The final product is illustrated as Figure 1.3-10. Although relatively high-quality maps can be produced directly from Atlas GIS™ and a laser printer, significant graphical capabilities are added by the use of such programs as CorelDRAW®. Final maps produced in CorelDRAW® were outputted to a Matrix PRC film recorder (by Agfa) to make slides for presentations (Hartman and others, 1993; and in-house GIS presentations).

The above steps illustrate a simple, basic utility of GIS programming. Both the advantages and limitations of certain specific programs indicate that acquisition and testing of more analysis-oriented programming may be of value (see below). However, the relative power of a PC-based GIS program is clearly evident in maintaining geographically based information from a variety of sources and representing a number of different map scales, produced originally for different purposes spanning many years of research effort.

The second case study, concerning the Slope County area in southwestern North Dakota, employed similar and more advanced programming techniques. The structure of geological and paleontological databases maintained in Q&A® (e.g., *MNOS, *UNITS, *LOC, and *SPP) has been thoroughly reviewed (Hartman, 1992b, 1993). In summary, a relatively large number of surface and subsurface geological observations in the type area of the Slope Formation (1675 in Slope County and 423 in Golden Valley County) were entered in the *MNOS and *UNITS databases and subsequently digitized in Atlas GIS™. A selected aspect of this research was undertaken with Dr. Alan Cvancara of the University of North Dakota Department of Geology and Geological Engineering to provide a more rigorous basis for a temporal framework for the stratigraphic relationship between the coal-bearing strata and the inundations of the Cannonball Sea. This work represented the essence of coal-based data management for the purposes of coal correlation (Hartman, 1991). This project summarized the stratigraphic occurrence of coal-bearing strata relative to brackish water and freshwater fossil localities in over 110 sections and isolated geological observations. On the basis of the constructed stratigraphic framework 1) revised coal correlations were proposed, 2) coal bed nomenclature was revised, 3) the distribution of the tongues of the Cannonball Formation were graphically illustrated, 4) the tongues of the Cannonball Formation were named, and 5) the stratigraphic distribution of over 150 fossil localities was plotted, providing a temporal and environmental context for interpreting the geologic history of the area. Thus, this study provided a foundation for the stratigraphic and paleoenvironmental interpretation of lower and middle Paleocene coal-bearing strata in southwestern North Dakota.

As previously noted, Q&A® is a flat file database manager with some relational database capabilities through various report applications. To more fully utilize the potential of GIS technologies employing data maintained in Q&A®, database restructuring was instituted employing Access®, the fully relational database by Microsoft Corporation. In important ways, use of a fully relational database is a major departure from previously

Contour Interval = 20 ft

Figure 1.3-10. A structure contour map of the Williston lignite, Nesson Anticline area is displayed. The structure contour map of the base of the Williston lignite bed is overlaid on a cadastral base map, with political boundaries, transportation, hydrology, and geologic observations—all layers derived from GIS programming.

employed methods. The differences in data management philosophy between Q&A® and Access®, or any other relational programs, strongly influence database design and implementation. Access® was chosen over other relational databases because of its approach to queries and its full, nonproprietary programming language. Previous comments made on the ease of use of Q&A® for maintaining complex file structures are still valid (especially for the DOS Version 4.0). However, when disparate data types (e.g., geologic locations and bed names) need to be brought together to form a combined query (as in one to many), relational file structure provides an inherently better approach. As an example, the revision and reformatting of the *LOC and *SPP database structures from Q&A® to Access® is discussed in the following paragraphs. Similar revisions were also undertaken in the *MNO and *UNITS databases, as noted below.

The Q&A® *LOC database consists of thousands of localities with information on the timing of coal deposition. The database contains over 100 fields concerning reference, location, stratigraphy, discovery, collection, and associated information. The revised Access® database consists of one main database (LNO.MDB), with a number of tables (containing related fields) and a few associated attached tables from other databases (e.g., MAPS.MDB). The database is controlled by a primary form based on a primary table ("LnoPri"). Other related tables, which can be accessed independently within the database, have subforms within the primary form. As implied by the name, the "LnoPri" table includes the primary record of locality number (unique Lno) (Figure 1.3-11). A primary record consists of the best (i.e., current) interpretation of a geographic occurrence of a locality. Previous interpretations, which may be thought of as a history of the locality, are stored in the "LnoHist" table. The structure of two tables is identical, except that the Lno is the key field (i.e., unique and indexed L-numbers) in the "LnoPri" table. A key field requires that each entry (such as locality number) be unique, and thus only one location can exist for each locality in the table. A history table ("LnoHist") does not require the Lno to be unique, in that it will not be used to establish a one-to-many relationship with other tables. Thus, multiple references to the same locality can be incorporated in the "LnoHist" table to track on the reporting history of the locality.

Important associated tables are directly related to the "LnoPri" form. These tables include information on stratigraphy ("LnoStrat" and "LnoMarker"), institutional representation ("LnoInst"), personnel ("RefBoss"), sample discovery ("LnoDisc"), sample collection ("LnoColl"), faunal content ("LnoFauna"), and other topics. All of these tables can be queried from the primary form ("LnoPri") as necessary. In addition, other information, such as map data (MAPS.MDB), previously included in the Q&A® *LOC database, as part of an external lookup table, are now maintained in their own databases and are attached to the Access® LNO.MDB database and used in the "LnoPri" form. The difference and main advantage of Access® over Q&A® is that there is essentially no duplication of data in the table structure. In Q&A®, certain information is duplicated in fields from one entry to another to allow for sorts of all types of information within one form design. Another advantage is that dBASE® file formats can be read and used directly by Access® without importing (e.g., dBASE® files in Atlas GIS™). Disadvantages of using Access® include a more complex form and subform structure and query and report writing procedures. In addition, data mergers (like mail merge) capabilities to additional form designs are presently not available in Access®.

The main advantage of Access® over Q&A® is, however, the addition of tables and forms from other databases to permit direct relational queries and reports. This ability is

Access® Locality Database Management

Figure 1.3-11. Access® locality database management. File names SPP.MDB and MAPS.MDB are databases attached to database LNO.MDB, which contains several tables that can be shown in any number of form and subform configurations.

not present in Q&A® as a flat file manager. At present, the main database related to *LNO.MDB concerns species identification (SPP.MDB). This database is related through an "attached" table ("SpeciesIdent") to LNO.MDB. With an identification table attached to the locality database, a query requesting the distribution of identifications in time and space of species records can be constructed.

To produce a GIS plot of the localities or a plot of a selected identification from a set of localities, an appropriate Access® query is written that creates a new table structure to be exported for use by Atlas GIS™ (see Figures 1.3-12 and 1.3-13 and Table 1.3-1 for illustrations and descriptions of this procedure). Basically, this query is similar to exports from Q&A®. Atlas GIS™ produces a plot of the localities. Figure 1.3-14 illustrates the distribution of all of the L-numbered (Lno) localities in a reach of the Little Missouri River in northern Slope and southeastern Golden Valley Counties. The distribution of a taxon, *Viviparus meeki* (Meek and Hayden) was selected from these L-numbered localities to be portrayed as shown in Figure 1.3-15. With an understanding of the geology (not portrayed on this map), Figure 1.3-15 shows a restricted distribution relative to the plot of all of the localities (Figure 1.3-14). The record of this taxon, as shown here, is temporally significant. The occurrence represents a distribution above the Yule lignite bed in the upper part of the Slope Formation and into the Bullion Creek Formation. The timing is at the onset of thick coal deposits, in part represented by the Hanson and Harmon lignite beds.

Following a similar methodology, the data in *MNOS and *UNITS databases, maintained in Q&A®, were used in Access® to query directly the distribution of lignite beds in time and space. These derived tables were used in Atlas GIS™ to produce geologic observation and lignite distribution maps. The results of this process are shown in Figures 1.3-16 and 1.3-17. The distribution of M-numbered (Mno) observations was plotted along the same reach of the Little Missouri River as shown in the Lno locality maps. In Figure 1.3-17, the distribution of the Yule lignite bed, an important local bed, is selectively plotted. A correlation diagram showing the stratigraphic relationships of the coal-bearing strata in this area is shown in Figure 1.3-18. With the coal bed correlations interpreted employing the database structure described above, any of the lignite beds found in the test area could be so plotted and used in resource assessment and characterization.

The approaches to GIS described above represent a first step toward full implementation of GIS capabilities at the EERC. The methods employed here represent various means to portray map information in a way that is convenient and relatively easy to produce compared to conventional map production. However, the analysis capabilities of PC-based GIS programming are limiting in a number of important ways. The lack of relational database capabilities prohibits the actual analysis of data. Certain types of questions simply cannot be asked. These questions concern the fundamental utilization of geologic information for resource assessment concerns. Future studies will develop applications on a UNIX operating system employing fully relational GIS programming (e.g., ARCINFO® by Environmental Systems Research Institute, Inc.).

In summary, a GIS approach to data management will become integral to any research undertaking that requires the synthesis of information across disciplines. The proviso that this information be map-oriented, that is, tied to a point or area on the earth, encompasses essentially all but the most conceptual problems. A GIS approach, however, is more complicated in its relational data management and more expensive than many

Figure 1.3-12. Creating a GIS map – processing flowchart.

Figure 1.3-13. Creating a GIS map – an example.

TABLE 1.3-1

**Creating a Map of the Geographic Distribution of
Geological Observations with Atlas GIS™ and Access®**

From the Q&A® *UNITS File

- **Export, to a Paradox® or dBASE® file format, all of the geologic units for a particular study area (Figures 1.3-12a and 1.3-13c). To restrict the geographic area selected for plotting, an external lookup programming statement is used to relate the UNITS observations to the geographic fields (e.g., state, county, township) in the MNOS database. This operation is only meaningful where a bed name is entered in the BED field in the Q&A® UNITS database. The following fields were exported for the example given in Figures 1.3-14–1.3-17: Mno (M-number), U# (section unit number), BED (bed name), Tk/m (unit thickness in meters), and DESC (bed description).**

In Access®

- **Create a new database or open an existing one in Access® and import the Paradox® or dBASE® file created in Q&A®. The import process creates a new table in the current database (Figure 1.3-12c).**
- **Attach the Atlas GIS™ dBASE® (attribute) file associated with the appropriate Atlas GIS™ geographic file (Figures 1.3-12d and 1.3-13a and b). Figures 1.3-12d ("int") and 1.3-13a represent the original Atlas GIS™ geographic file constructed through the process of digitizing of a location locality from a topographic map. This file contains the unique ID number (assigned by Atlas GIS™ to the digitized Mno location) and the latitude and longitude of the location. The Atlas GIS™ attribute file (Figure 1.3-13b) is attached to an Access® database as illustrated in Figure 1.3-12d–e.**
- **A query in Access® is then designed to create a new table (Figures 1.3-12e and 1.3-13d) based on a relationship between the table containing the imported bed names (Figure 1.3-12b) and the attached attribute file (Figure 1.3-12d). The selection criterion in the query table is the name of the bed or beds will be plotted. The resulting tables contain only the unique ID assigned by Atlas GIS™ for the Mno that contains the requested bed names (Figure 1.3-13e).**
- **The selection criterion for plotting the new Access® query table is then exported as a dBASE® file to the directory where the Atlas GIS™ geographic and attribute files are stored.**

In Atlas GIS™

- **Load the Atlas GIS™ geographic file of interest (Figure 1.3-13f) and specify the attribute file to use as the newly exported query table from Access® (Figures 1.3-12f and 1.3-13e). Atlas GIS™ automatically matches the unique ID number in the attribute file with the identical number in the geographic file (Figure 1.3-13g).**
- **If the Atlas GIS™ "layer" settings are set as to show all the Mno locations in a particular area, a subset of those locations can be selected based on whether or not an attribute value is associated with the geographic ID. This subset of points is then copied to a separate geographic layer and depicted in whatever manner is desired (Figure 1.3-12g).**
- **Finally, for the purposes of this report, the resulting map is exported from Atlas GIS™ as a CGM file type to be imported and subsequently embellished in CorelDRAW® (Figures 1.3-12g and 1.3-14–1.3-17).**

Figure 1.3-14. Map of the distribution of fossil localities in the Brown Ranch test case area.

Figure 1.3-15. Map of the distribution of the mesogastropod snail *Viviparus meeki* (Meek and Hayden) in the Brown Ranch test case area.

Figure 1.3-16. Map of the distribution of surface and subsurface geological observations in the Brown Ranch test case area.

Figure 1.3-17. Map of the distribution of surface geological observations on the Yule lignite bed in the upper part of the Slope Formation in the Brown Ranch test case area.

Stratigraphy of the Ludlow and Slope Formations in the Vicinity of Township T. 135 N., R. 105 W., Slope County, North Dakota

Figure 1.3-18. Correlation diagram of the coal-bearing strata in the type area of the Slope Formation, Slope County, North Dakota.

other tools in a computer's arsenal to manipulate information. The market for GIS is changing rapidly as many local, state, and federal agencies commit to a strategy of managing the resources under their charge through GIS technologies. With this commitment, new opportunities will exist that permit a far greater utilization of existing information and thus provide a means for more rigorous and soundly based resource decisions.

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TASK 1.0 RESOURCE CHARACTERIZATION AND RESIDUAL REMEDIATION

Subtask 1.5 Supplemental Research Related to the Rocky Mountain 1 Underground Coal Gasification Test Program

INTRODUCTION

As part of a long-term, multiactivity research effort related to the Rocky Mountain 1 (RM1) underground coal gasification (UCG) test program, the Energy & Environmental Research Center (EERC), initially with funding from the Gas Research Institute (GRI) and more recently with funding from both GRI and the U.S. Department of Energy (DOE) 1) monitored, on a periodic basis, overburden and groundwater temperatures at the RM1 site and 2) mineralogically and chemically characterized test-related, thermally altered solid materials from the RM1 site.

The immediate goal of both activities was to generate data that would contribute to the characterization of the thermal impacts resulting from the demonstration of the two UCG technology variations that were the focus of this program. At the same time, the resulting data were intended to be utilized, in conjunction with other site- and test-related data, to develop the understanding of UCG-related process-setting interactions that is critical for significantly improving the design, siting, conduct, and evaluation of future UCG operations.

Specifically, with respect to the first noted initiative, thermal data acquired during the three years following the test itself indicated gradual, continuous temperature increases of 6° to 10°C in an 8-meter-thick section of overburden at distances of about 10 meters from each of the two test cavities. The data, which were obtained periodically from the extensive network of groundwater monitoring wells on the site, also provided evidence for temperature increases of up to 12°C in a 60-meter-thick section of overburden at a distance of about 100 meters in one direction from the cavities. Subsequently, available PC-based capabilities were utilized to develop a two-dimensional numerical model of the test-related hydrothermal regime at the site. Although the modeling was necessarily on a coarse-dimensional scale (one meter) and was therefore limited in its resolution of the local hydrothermal regime, the modeling results indicated that the observed temperature increases were caused by heat transport in groundwater flowing in permeable sections of the overburden and in the coal. This provided additional evidence that the UCG test burn functioned as an open system that included the groundwater in the vicinity of the test cavities. At the same time, the modeling results raised questions as to whether residual heat in and near the test cavities was sufficient to account for the temperature trends observed during the posttest period.

In spite of the utility of this modeling effort, the fact that it was necessarily done on a coarse-dimensional scale limited the detail with which the local hydrothermal regime could be reconstructed and did not allow for resolving the heat source issue. In effect, the effort fell well short of maximizing the utility of available thermal data. The recent acquisition of a CRAY X/MP supercomputer system by the University of North Dakota (UND) College of Aerospace Sciences has provided an opportunity to cost-effectively undertake the fine-scale (centimeter-scale) modeling that will enable all of the noted data to be used to much more accurately represent the nature of heat flow in and around the test cavities in the context of the transient conditions that characterized the RM1 site

during the test and posttest periods. At the same time, the advanced capabilities provided by the CRAY system allow the heat source issue to be effectively addressed.

With respect to the second noted initiative, that is, the characterization of test-related, thermally altered solid materials from the RM1 site, the various activities that have been undertaken by the EERC over the last several years to achieve this goal have resulted in very large amounts of data related to the approximately 70 mineral and amorphous phases that have been identified. As envisioned, these data have proven to be an invaluable resource in furthering our understanding of UCG process:setting interactions, and, as such, have ensured that decisions regarding future UCG operations will be much more soundly based. At the same time, much has been learned about the best ways to generate and interpret such data, thus increasing the utility of characterization activities to those UCG efforts that follow. The nearly completed draft report reviewing the design, conduct, and results of the noted RM1 characterization activities does not allow for the incorporation of much of this very useful knowledge base, thus presenting the possibility that the data will remain inaccessible unless they can be made available by another means.

In an effort to address this problem, the decision was made to develop an "atlas" of the mineral and amorphous phases identified during the course of the RM1-related characterization work. This document is intended to provide those involved in UCG research and development, as well as those in other disciplines for whom this work may have some relevance (for example, ceramics), with documentation that will allow the rapid identification and interpretation of the noted phases. Specifically, the "atlas" will include, for each phase:

- Key identification criteria for the most applicable analytical techniques, suitably supported by selected data and photomicrographs.
- Information on occurrence of the phase in the RM1 thermally altered materials, including the form(s) it takes, the frequency of its occurrence, and the phases with which it is associated.
- Comments on the origin of the phase at the RM1 site.
- A brief summary of the primary implications of the phase in a UCG context.

OBJECTIVES

The current work introduced above will allow two primary focuses of the EERC RM1-related research effort to be brought to a satisfactory conclusion, producing results of critical importance to the successful culmination of the RM1 test program, as well as to those involved in future UCG research and development efforts. Specifically, the objectives of this work, which was initiated in August, 1993, and will be concluded at the end of August, 1994, are as follows:

- To more rigorously analyze the UCG-related hydrothermal regime at the RM1 site using advanced computer capabilities applied to all relevant available thermal data (Subtask 1.5.1).

- To develop an "atlas" of mineral and amorphous phases identified in the thermally altered solid materials from the RM1 site (Subtask 1.5.2).

ACCOMPLISHMENTS

Subtask 1.5.1

Dr. W.D. Gosnold (UND Department of Geology and Geological Engineering) continued to be responsible for this effort on behalf of the EERC, most recently with the help of Mr. Sameer Padhye, a graduate student, who will use his participation in the Cray modeling as the basis for a Master of Science thesis in computer science. During the report period, Dr. Gosnold and Mr. Padhye accomplished the following:

- Completion of the transformation of the PC-based computer code that was developed to initially analyze the RM1 hydrothermal regime. This effort specifically involved translating the code from Fortran 90 to CF77 for use on the UND Cray X/MP supercomputer system.
- Successful compilation of the transformed model on the Cray system.
- Completion of the initial execution of the model on the Cray system.
- Initiation of the refinement of the model in an effort to ensure that 1) the physical phenomena related to the RM1 hydrothermal system are simulated as accurately as the available data allows during the upcoming detailed analysis and 2) the simulation process is as efficient as possible. This preliminary work included 1) standardizing the input files to overcome problems encountered in reading long input records and 2) activities focused on parallelizing and vectorizing to reduce the execution time of the model.
- Initiation of an evaluation of available visualization programs in the Cray system for possible application in conjunction with the model in question.

Additional activities related to this initiative during the report period include the following:

- Mr. Padhye's attendance at Supercomputing '93, a major supercomputing conference held in Portland, Oregon. In response to the needs of this effort, Mr. Padhye 1) participated in a one-day visualization tutorial, 2) attended several papers on scientific applications of Cray supercomputers, and 3) investigated a promising option for implementing visualization routines for the model that is the focus of these activities.
- Preliminary discussions among participants in the EERC's RM1-related research efforts regarding the issue of heat sources for the hydrothermal system being modeled. Now that the model is operable on the Cray system, activities related to modeling alternative heat sources will begin in earnest. In this regard, extensive discussions with John Boysen (Resource Technology Corporation, Inc.), who has been working on the RM1 material and energy balances on behalf of the

EERC, are critical. It is expected that these discussions will take place when Mr. Boysen visits the EERC early next quarter.

Subtask 1.5.2

Professor R.A. Kühnel (International Institute for Aerospace Survey and Earth Sciences), together with Tina Strobel and Kurt Eylands of the EERC, continued to be responsible for this effort. Professor Kühnel visited the EERC from October 2-23, during which period he worked primarily with the noted EERC project participants to accomplish the following:

- Finalize the work plan, including assignments and schedule, for the activities leading to the completion of the "atlas."
- Complete a draft outline of the "atlas," as well as several sample sections treating individual phases, for eventual submission to the USDOE and GRI for their review.
- Review available characterization data and photomicrographs for inclusion in the document.
- Plan for selectively generating required illustrative material where appropriate data and photomicrographs are not presently available.

Subsequent to Professor Kühnel's visit the following activities took place:

- The draft outline of the "atlas" and the completed sample sections were reviewed in-house and revised in response to those reviews. Submission of the draft for DOE and GRI review has been delayed as the result of difficulties encountered in getting final approval of the revisions from Professor Kühnel, who has been traveling extensively in Europe and Southeast Asia.
- Illustrative data and photomicrographs continued to be reviewed for inclusion in the "atlas."
- Preliminary drafts of about 20 additional sections treating individual phases were completed and their revision for in-house review was initiated.

Air Quality Assessment and Control
Task 2.0

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EXECUTIVE SUMMARY

Emissions of fine particles are of concern because these particles can be deposited in the lower respiratory system through normal breathing. The potential 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 the potentially most hazardous particles from coal combustion are collected with the lowest removal efficiency. The 1990 Clean Air Act Amendments address the issue of emissions of acid rain precursors, require the study of air toxic emissions, and provide for possible expansion of visibility protection measures. Therefore, a current need exists to develop superior, but economical, methods to control emissions of air toxic particulate matter. One approach is to model the relationships between the cohesive properties of fly ash and particulate collector performance in electrostatic precipitators (ESPs) and fabric filters. In ESPs, a balance between good dust release and minimum redispersion must be achieved for optimum ESP fine-particle collection efficiency. To achieve high fine-particle collection efficiency with fabric filters, the large pores in the fabric must be adequately bridged, and reentrainment must be kept to a minimum while still allowing for adequate dust cake release. However, the defining relationships between cohesive dust properties and particulate collector performance have not been adequately developed.

Therefore, the goal of the Fine Particulate Control project is the development of methods to measure the cohesive strength and reentrainment potential of fly ashes and to model emissions of fine particles based on these measurements. A long-term project goal is to develop the models to the point where they can be used to help design particulate control devices for the lowest level of fine-particle emissions at a reasonable cost.

Recent results show that tensile strength, aerated porosity, and packed porosity measurements are appropriate methods to quantify the cohesive properties of fly ash. Fly ashes with tensile strengths of less than 50 N/m^2 are likely to have significantly greater ESP rapping dispersion of fine particles than fly ashes with tensile strengths greater than 250 N/m^2 . Fly ash tensile strength also appears to be a good predictor of fabric filter particulate emissions. Fine-particle emissions from a pulse-jet baghouse with Ryton felted fabric were 100 times greater for a fly ash with a tensile strength less than 100 N/m^2 compared to fly ashes with tensile strengths greater than 250 N/m^2 . In direct pore-bridging experiments with monosized openings, tensile strength was found to be an indicator of maximum bridging velocity. In tests with pulse jet-cleaned Ryton bags, packed porosity was a good indicator of initial or effective K_2 . Bench-scale tests, however, have shown that particle size and face velocity must also be incorporated into a model to predict pressure drop as a function of dust properties. Reentrainment tests indicate that velocity is an important parameter affecting pore-bridging ability and the occurrence of reentrainment. Future efforts will attempt to incorporate particle size and velocity into a more general model.

TASK 2.0 AIR QUALITY ASSESSMENT AND CONTROL

Subtask 2.2 Fine Particulate Control

INTRODUCTION

The Air Quality Assessment and Control project category consists of three tasks as presented in the Annual Project Plan:

Task 2.1: Air Toxics

Task 2.2: Fine Particulate Control

Task 2.3: Novel Flue Gas-Cleaning Methods

Only Task 2.2, Fine Particulate Control, was funded for 1993, and so the report for Task 2.0 summarizes work in the fine particulate control area only. This report consists of the semiannual report for July through December and a topical report for the entire year.

Background

Emissions of fine particles are of concern because these particles can be deposited in the lower respiratory system through normal breathing. The potential 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 the potentially most hazardous particles from coal combustion are collected with the lowest removal efficiency. In addition to potentially causing adverse health effects, fine particles, including secondary sulfates, are the primary cause of visibility impairment in the atmosphere. The 1990 Clean Air Act Amendments address the issue of emissions of acid rain precursors, require the study of air toxic emissions, and provide for possible expansion of visibility protection measures. The American Lung Association has joined in a lawsuit to force the Environmental Protection Agency to expedite its review of the national ambient air quality standard for particulate matter (PM₁₀) due to concerns that the current standard may not adequately protect public health. This lawsuit was prompted by a recent study that attributed 60,000 deaths per year to fine particulate levels that are within the current standard (1). Therefore, a current need exists to develop superior, but economical, methods to control emissions of SO₂, NO_x, and air toxic particulate matter.

Previous research at the Energy & Environmental Research Center (EERC) has focused on two areas: 1) bench-scale efforts to investigate the relationships between fine-particle emissions from fabric filters or electrostatic precipitators (ESPs) and the cohesive properties of fly ash and 2) investigation of the impact of coal combustion on atmospheric visibility. Control of fine-particle emissions from coal-fired boilers is an issue because of the current concern over atmospheric air toxics, which contain high concentrations of trace elements. The best method of minimizing the emission of these air toxic trace elements to the atmosphere is to install high-efficiency fine-particle control devices. Previous research has shown that the collectibility of fine particles from coal combustion is highly dependent on the cohesive properties of the fly ash. Therefore, past research has focused on quantitative measurements of cohesive properties of fly ash and filtration behavior. The goal is to achieve the lowest level of fine-particle emissions,

without an economic penalty, either by modifying the ash properties or by other design optimization methods. Significant progress has already been made toward this goal, but further bench-scale work is needed to develop and test models that predict fine-particle emissions based on ash properties.

OBJECTIVES

The goal of Task 2.2 is the development of methods to measure the cohesive strength and reentrainment potential of fly ashes and to model emissions of fine particles based on these measurements. Past research has concentrated on development of reliable methods to measure the cohesive properties of fly ash. While further refinement of these methods is desirable, they are already developed to the point where they can be used for modeling efforts. Therefore, the primary goal of the fine particulate control task for the 1993 project year was to develop a preliminary model that relates cohesive properties to fine-particle emissions and one that relates cohesive properties to flow resistance. The primary elements of the models will include tensile strength, porosity, particle size, pore-bridging ability (or, conversely, reentrainment potential), and face velocity. A long-term project goal is to develop the models to the point where they can be used to help design particulate control devices for the lowest level of fine-particle emissions at a reasonable cost.

ACCOMPLISHMENTS

Scope of Work

The planned scope of work consisted of bench-scale experiments to measure the cohesive properties of fly ash samples, bench-scale pore-bridging/reentrainment tests, and efforts to develop models based on both previous and new data.

Procedures were already developed to measure cohesive fly ash properties from previous work, but tests had been completed with only a limited number of ash samples. Additional fly ash samples tested this year were selected from our stored fly ash sample inventory, based on previous fabric filtration experiments at the EERC. Some new fly ash samples were available from another project at the EERC and were tested for cohesive characteristics. In addition, the cohesive properties of two PFBC fly ash samples received from METC (generated at the Karhula and Tidd plants) were tested. The cohesive measurements consist of tensile strength tests, conducted with a Cohetester, and aerated or packed porosity measurements, conducted with a powder characteristics tester.

The pore-bridging/reentrainment tests consisted of filtration tests with precision metal electroformed sieves of exact pore dimensions. The dust for these tests was dispersed with a dry powder disperser, and particulate emissions were measured downstream of the filter with a laser particle sizer. Visual observation of the clean and dirty sides of the screens provided information on the conditions when complete pore bridging occurred or when reentrainment occurred.

Modeling work consisted of efforts to correlate particulate emissions with cohesive dust properties and analysis of the primary parameters that must be included in a more

comprehensive model. The goal of the model is to predict fine-particle collection efficiency and pressure drop as a function of fly ash tensile strength, aerated and/or packed porosity, particle size, pore-bridging ability (or, conversely, reentrainment potential), and face velocity. Other possible model inputs may eventually include chemical composition, particle morphology, and specific surface area. Model development must follow a logical progression, starting with the parameters that are known to have major effects, and then progressing with inputs from the minor effects. While some progress was made toward the modeling goal, the work is very preliminary and much additional work will be required to develop good predictive models.

Preliminary Modeling Efforts

The Need for a Model Relating Particulate Emissions to Dust Characteristics

Recent concern about fine-particle air toxic emissions has generated renewed interest in economical methods to improve fine-particle collection efficiency of both ESPs and baghouses. One approach is to model the relationships between the cohesive properties of fly ash and particulate collector performance. Cohesive properties of fly ash have been known for many years to influence the collectibility of fly ash in ESPs. White (2) devotes a whole chapter in his book to reentrainment effects in ESPs, but does not identify a specific dust characteristic that influences the level of reentrainment. Dismukes (3) identifies a change in fly ash cohesiveness as one of the mechanisms by which conditioning agents improve ESP performance, but does not present any quantitative data on the cohesive properties of fly ash. Spencer (4) identifies fly ash tensile strength as an important consideration in the study of ESP rapping, but does not relate tensile strength to any specific performance data. Particle adhesion was recognized by Billings and Wilder as an important parameter affecting fabric cleanability (5) and Dennis and coworkers stress that cohesive fly ash properties are important to fabric filter performance, but did not incorporate these properties into their filtration model (6). More recently, Bush and coworkers (7) have identified cohesivity as the primary ash characteristic affecting baghouse pressure drop and have presented effective angle of internal friction and compacted porosity as quantitative laboratory measurements of cohesive fly ash characteristics. Bush and coworkers correlate effective angle of internal friction and compacted porosity with residual dust cake weight for a narrow data set of baghouses with reverse-gas cleaning and woven glass fabric. No attempt was made to correlate particulate emissions with cohesive characteristics. We have previously emphasized the importance of cohesive dust properties in the study of how conditioning can be applied to fabric filters to improve performance (8, 9). However, the defining relationships between cohesive dust properties and particulate collector performance have not been adequately developed.

In ESPs, an ideal dust would readily release from the plates upon rapping and fall to the hopper with minimum redispersion. Cake release, rapping reentrainment, and hopper reentrainment are all likely to be impacted by the cohesive properties of the dust. To achieve good dust cake release, a minimum cohesive or tensile strength would appear desirable, but to minimize redispersion of the dust into its original particle-size distribution, high dust tensile strength is preferred. Since these two factors are in direct opposition, a balance between good dust release and minimum redispersion must be achieved for optimum ESP performance.

Fabric filter performance is also impacted by cohesive dust properties. Since most fabrics have significantly larger pore sizes than the median particle size of the collected dust, high particle collection efficiency cannot occur unless the pores are effectively bridged. If pores are not adequately bridged, high-velocity pinholes can develop in the dust cake, leading to poor collection efficiency. Ideally, starting with a new fabric, the large pores should be bridged in the first filtration cycle and then remain bridged when the bags are cleaned. If emission spikes occur after bag cleaning when many of the larger pores are opened, the pores must be bridged over again during each cleaning cycle to maintain a high collection efficiency. To achieve good pore bridging in fabric filters, high cohesive strength would appear to be desirable.

Independent of the pore-bridging ability of the dust is the cake-release character of the dust cake. The cake should release from the fabric with minimum energy input, without significant redispersion of the dust, while maintaining some minimum residual dust cake to help achieve a high collection efficiency. The relationship between cohesive dust properties and collection efficiency in a fabric filter is analogous to that in an ESP. In both cases, the dust must be low enough in cohesive strength to release readily, but high enough in cohesive strength to minimize reentrainment. However, with fabric filters the impact of cohesive dust characteristics on performance is more complex, because the cohesive properties are also likely to have a major effect on pressure drop. Besides particle-size effects, the primary cake properties that determine pressure drop are the cake porosity and thickness. Low cohesive strength appears to facilitate good cake release and low residual dust cake thickness, while high cohesive strength seems necessary to maintain a high dust cake porosity and prevent significant dust cake packing. Obviously, there must be a proper balance between these factors to optimize both particulate collection efficiency and pressure drop in fabric filters.

The cohesive properties of fly ash are important to the optimization of ESP and fabric filter performance. However, cohesive strength, along with other similar terms such as cohesivity and cohesiveness, is not well defined. Therefore, the first step to optimize collector performance is to select key cohesive characteristics that are well defined and can be quantitatively measured. Tensile strength and aerated or packed porosity are two such quantitative measurements. We have previously presented extensive data on the tensile strength and porosity of fly ash and present in this report initial correlations between these properties and control device performance.

Measurement of Cohesive Fly Ash Properties

Previous attempts to quantitatively measure cohesive properties of powders included the Jenike flow-factor tester and a tilting table apparatus. Several shear methods have also been used to measure the flow properties of bulk solids. One shear method is the rotational ring shear device, which Southern Research Institute has used to measure cohesive properties of fly ash (10). From the ring shear data, the effective angle of internal friction was selected as the most useful parameter, with typical values ranging from 31° to 47° for coal fly ash. One apparent disadvantage of the ring shear method, however, is that the porosity of the shear layer is generally not known. More recently, Pontius and Snyder reported that an electrostatic tensiometer can measure the tensile strength of powders by exposing a sample of the powder to an electrostatic field generated in a parallel-plate electrode system (11). Tensiometer-determined tensile strengths for

powders, including fly ash in the range of 1 to 15 N/m², appear to be somewhat lower than fly ash tensile strengths reported for other methods.

Initial development of an instrument to directly and quantitatively measure the tensile strength of powders occurred in the early 1960s at Warren Spring Laboratory in England (12). In the Warren Spring Laboratory apparatus, a powder sample was compacted under a controlled normal load into a cylindrical cell that was split diametrically. This apparatus served as the basis for the development of a commercially available instrument, called a Cohetester, which directly measures the tensile strength of bulk powders as a function of compaction pressure and is commercially available from Hosokawa Micron International, Inc. Yokoyama and Fujii reported tensile strengths for bulk powders in the range of 18 to 440 N/m² in developmental research for the Cohetester (13). Since we have previously presented extensive data obtained at the EERC with the Cohetester, no further discussion on the Cohetester is given here (14, 15).

Since dust cake porosity will have a major effect on baghouse pressure drop, a direct determination of fly ash porosity in the laboratory would appear to be a relevant measurement. ASTM standard test methods for determination of the tap density of refractory metal powders (B527) and for determination of tapped packing density of catalyst particles (D4164) are possible measurements that could be applied to fly ash. Both methods are straightforward in that a bulk sample is placed in a glass graduated cylinder, which is tapped either 1000 (D4164) or 3000 (B527) times. The volume after tapping and sample weight provide the information to calculate the tapped density. Quantachrome Corporation manufactures an instrument called the Dual Autotap which conforms to ASTM standard test procedures B527 and D4164. These ASTM methods have not been applied to fly ash, but could be if appropriate sample preparation methods were added to the procedures.

For determination of the packing properties of fly ash, we selected an instrument called a Powder Characteristics Tester, also available from Hosokawa Micron International, Inc. Again, we have previously reported extensive aerated and packed porosity data obtained with this instrument and discussed experimental procedures (15, 16). The aerated bulk porosity represents the maximum porosity at which the dust sample can support itself. The packed porosity values appear to be a good indication of the tendency of the fly ash to pack under dust cake conditions, which means that packed porosity might be used to predict pressure drop. While many researchers have discussed cake collapse as a possible result of increased pressure drop, Schmidt and Löffler (17), by looking at porosity as a function of cake depth, quantified the effect. Packed porosity values as low as 31% have been measured for a fairly noncohesive fly ash, reflecting the potential of the dust cake to collapse under increased pressure drop and repeated bag cleaning. The aerated porosity, however, is more indicative of the initial porosity of the dust layer as it originally developed.

Both the tensile strength and aerated or packed porosity measurements appear to be good methods to quantify the cohesive properties of fly ash. A question exists as to whether the tensile strength and porosity measurements are simply different methods of determining the same cohesive characteristic; however, Figure 1 indicates that since there is not a good correlation between tensile strength and aerated or packed porosity, the two

Figure 1. Correlation between aerated or packed porosity and tensile strength.

measurements provide independent information. Even though these measurements look promising, a consensus needs to be formed to standardize measurements and procedures for determination of cohesive fly ash properties.

Correlation Between Rapping Reentrainment and Tensile Strength

The focus of the project is to model the relationships between dust properties and fabric filter performance. However, some of the same dust characteristics that affect fabric filter operation will also affect ESP performance. Results that were available from an ESP conditioning project are presented here because they help to provide a better understanding of how cohesive dust properties affect particulate collector performance in general. A pilot study was conducted at the EERC to evaluate enhanced flue gas conditioning methods for improving ESP performance for Wahlco, Inc., and the U.S. Department of Energy (DOE) (18, 19). Since one of the mechanisms of performance improvement with conditioning agents was known to be changes in cohesive dust properties, the tensile strengths of conditioned and baseline ESP hopper ash samples were measured with the Cohetester. Tests were conducted with a pilot-scale pulverized coal-fired combustor and a single-wire tubular ESP that had a plate length of 79 in. and an inside diameter of 8.3 in. The gas velocity through the ESP was held constant at 5 ft/sec, giving a specific collection area (SCA) of 124 ft²/1000 acfm. Respirable mass particulate emissions were measured continuously with a TSI model APS 33 laser particle sizer. Respirable mass is defined by the American Council of Governmental and Industrial Hygienists as a weighted sum of particles between 1 and 10 μ m, with greater weighting given to the smaller particles. Rapping reentrainment was not a primary focus of the

study, but rapping emissions data were taken for a variety of conditions since the APS could quantify very short emission spikes. Respirable mass rapping emissions as a function of maximum tensile strength (i.e., the tensile strength measured at a maximum compaction of $2.5 \times 10^4 \text{ N/m}^2$) are shown in Figure 2 for a West Virginia bituminous coal. Tensile strengths were altered by injecting varying amounts of ammonia and SO_2 as dual conditioning agents into the flue gas upstream of the ESP. The lowest tensile strengths occurred for baseline tests with no conditioning. Note that there was a two-orders-of-magnitude decrease in rapping emissions with an increase in tensile strength. At the higher tensile strengths, there was no measured increase in respirable mass emissions with on-line rapping over the background emissions, even though ash was removed from the plate. This implies that particles in the 1- to $10\text{-}\mu\text{m}$ range were not redispersed as individual particles, but remained as large agglomerates that easily reached the hopper. On the other hand, the data indicate that for low-tensile-strength dusts, particles are readily redispersed as individual particles with rapping. To achieve low emissions with a very low-tensile-strength dust would require a much larger ESP with more fields. The data indicate that dusts with a tensile strength less than 50 N/m^2 are quite susceptible to particle redispersion and that dusts with a tensile strength of 500 N/m^2 will have minimal fine-particle reentrainment. The data also suggest that no further benefit is seen when the tensile strength is increased beyond 500 N/m^2 . Caution must be emphasized that the relative value of the rapping emissions is more important than the absolute value of the emissions, because of the significant differences between a full-scale ESP and the pilot-scale system. The data do show, however, a quantitative relationship between the level of fine-particle rapping reentrainment and fly ash tensile strength and suggest that

Figure 2. ESP rapping reentrainment of respirable mass particulate emissions as a function of fly ash tensile strength.

knowledge of the tensile strength of fly ash might be used to improve ESP performance, either by design changes or by the use of conditioning agents.

Correlation Between Fabric Filter Emissions and Tensile Strength

Previous research at the EERC investigating methods to improve fabric filter performance by flue gas conditioning has shown that the conditioning process significantly changes the cohesive properties of fly ash (8, 9). In general, the conditioning increases the tensile strength at constant porosity, which indicates that there is an increase in particle-particle binding forces. While the evidence is strong that particulate emissions are related to the cohesive characteristics of the dust, a quantitative relationship between emissions and any well-defined cohesive measurement has not previously been developed. In addition to cohesive fly ash properties, fabric filter emissions will depend on particle size, fabric pore size, fabric fiber diameter, bag-cleaning frequency, and face velocity. Therefore, the other variables should be held constant to evaluate particulate emissions as a function of cohesive properties.

A pilot-scale study was recently conducted at the EERC to evaluate the effectiveness of flue gas conditioning in reducing tube sheet pressure drop and fine particulate emissions from a pulse-jet fabric filter (9, 20). The project was jointly funded by DOE, the Electric Power Research Institute (EPRI), and the Canadian Electrical Association (CEA). The investigation included baseline tests and tests in which ammonia and SO_3 were injected upstream of the baghouse to determine the effect of conditioning on baghouse performance. The primary independent variables included coal type, conditioning agent concentrations, air-to-cloth (A/C) ratio, and fabric type. The main dependent variables were particulate emissions, baghouse pressure drop, and cohesive properties of the fly ash. Results demonstrated significant benefits of using conditioning with a pulse-jet baghouse, including a substantial reduction in particulate emissions and pressure drop (or the ability to operate at a higher A/C ratio without increasing pressure drop or bag-cleaning frequency). The improvements in fabric filter performance correlated strongly with a shift in the tensile strength and with increases in the aerated and packed porosity of the fly ash. Figure 3 provides a quantitative look at the relationship between tensile strength and fine-particle emissions for 100-hour pulse-jet tests with Ryton fabric and a constant A/C ratio of 4 ft/min. Average respirable mass emissions, measured with an APS 33 particle sizer, are plotted as a function of maximum tensile strength. Note that there was a two-orders-of-magnitude decrease in respirable mass particulate emissions as the tensile strength increased from about 100 to 250 N/m^2 , and no further decrease in emissions was seen with a further increase in tensile strength. The data indicate that dusts with a maximum tensile strength of less than 100 N/m^2 are more difficult to collect in a fabric filter; therefore, greater care must be taken with fabric selection, face velocity, and cleaning method to ensure a high collection efficiency with low-tensile-strength dusts. These fabric filter emission results are consistent with the ESP rapping reentrainment results in that dusts with tensile strengths lower than 100 N/m^2 present the greatest collectibility problem. This is not surprising because the level of dust redispersion is likely to contribute to high emissions in fabric filters as well as in ESPs. However, in fabric filters, the pore-bridging ability of the dust will also have an effect on particulate emissions. If the pore-bridging ability of the dust could also be predicted by the dust tensile strength, there would be even stronger evidence that tensile strength is a good indicator of dust collectibility in fabric filters.

Figure 3. Respirable mass particulate emissions as a function of fly ash tensile strength for 100-hour pulse-jet tests with Ryton fabric at an A/C ratio of 4 ft/min.

We have previously presented results from pore-bridging experiments with a bench-scale system consisting of an 8- x 8-in. filter and a dry powder disperser to introduce the fly ash into the carrier gas upstream of the filter (15, 21). Tests were conducted at ambient temperature without added conditioning agents under controlled relative humidities. Dust was introduced at a rate of 1.6 g/min for a period of 35 min, while particulate emissions and pressure drop were recorded as a function of time. Inspection of both the clean and dirty sides of the filters through sight ports gave visual proof of complete pore bridging or the formation of pinholes.

An initial test matrix was conducted at 10% relative humidity with five pore sizes: 300, 150, 75, 40, and 20 μm ; four face velocities: 1, 2, 4, and 8 ft/min; and two dust types: baseline and conditioned Monticello fly ash. The filters were precision electroformed nickel sieves, available from Buckbee-Meers, and had square openings. The data from this test matrix showed that conditioning, velocity, and pore size were critical parameters in predicting whether complete pore bridging will occur without reentrainment or pinhole formation. The data appeared to be well behaved in terms of establishing the maximum velocity at which bridging occurs for a given pore size, as shown in Figure 4. Results indicate that the effect of conditioning is to increase the range of pore size and velocities at which good pore bridging will occur. If pore size and velocity are kept below the maximum values shown, excellent collection efficiency should be achieved.

Pore-bridging tests were also conducted with the baseline and conditioned fly ash samples at 50% relative humidity. For the baseline ash, results showed that an increase

in relative humidity had very little effect on the maximum pore-bridging velocity. However, the pore-bridging ability of the conditioned ash was greatly improved at 50% relative humidity, as shown in Figure 4. These results are consistent with the tensile strength data. Increasing the relative humidity from 10% to 50% did not increase the tensile strength of the baseline ash but did increase the tensile strength of the conditioned ash. Maximum bridging velocity as a function of maximum tensile strength for the 150- μ m pore size is shown in Figure 5. Although only three data points were available, the data indicate that pore-bridging ability is predicted by tensile strength and that low filtration velocities are required to achieve high collection efficiency for dusts with tensile strengths less than 100 N/m². The bench-scale pore-bridging data and fabric filter emissions data provide strong evidence that tensile strength is a good predictor of dust collectibility in a fabric filter. The relationships are quantitative in that both emissions and maximum bridging velocity are given as a function of tensile strength. The usefulness of the correlations will depend on whether fabrics can be simulated by screens of exact pore sizes and whether other variables of interest such as porosity, particle size, velocity, cleaning methods, and cleaning frequency can be included in a more general model.

To further evaluate whether tensile strength might be a predictor of particulate emissions from a fabric filter, an old set of emissions data from a pilot baghouse with shaker-cleaned woven glass bags was explored (22). The data included tests with a number of different coals, and fly ash samples for many of the tests were available from storage at the EERC. The cohesive tensile strength of fly ash samples from these previous runs was measured using the Cohetester. The coals' inlet dust loading and

Figure 4. Effect of pore size on maximum pore-bridging velocity for screen tests with baseline and conditioned Monticello fly ash.

Figure 5. Maximum pore-bridging velocity for 150- μ m screen as a function of fly ash tensile strength.

particulate removal efficiency from these tests are listed in Table 1. The baghouse particulate penetration ranged from 0.1% to 24.0%. The extreme range in penetration values requires some explanation. The lowest penetration observed from these tests, 0.1% (99.9% removal efficiency), is consistent with the excellent removal efficiency expected with a baghouse. However, very high penetration levels in the range of 5% to 24% were measured for some tests. These high penetrations were the result of using a lightweight woven glass fabric, high air-to-cloth ratio of 3 to 4 ft/min, very vigorous shaker cleaning, and short-term tests. Nevertheless, the results demonstrated the wide range in emissions that could occur as a result of differences in ash properties. Tensile strength measurements, shown in Figures 6 and 7, were performed on some of these fly ash samples in an effort to see if there was a correlation between the tensile strength of the ash and particulate emissions. The fly ash samples were more than 10 years old and were stored in closed containers; however, some sample degradation due to oxidation or moisture may have occurred. The correlation between baghouse particulate emissions and tensile strength for these data is shown in Figure 8. With the exception of two outliers, the data suggest the same type of correlation that was presented in Figure 3. In both cases, the data indicate that as the tensile strength drops below 250 N/m^2 , a significant increase in particulate emissions will occur and that as the tensile strength is increased beyond 250 N/m^2 , emissions will level off to the point where no further benefit is seen with an increase in tensile strength. An explanation for the two outlying points is not clear other than possible sample degradation due to long-term storage. For example, the presence of moisture could facilitate slow hydration reactions on the fly ash surface which would likely change the cohesive characteristics. However, even if the outlying points are

TABLE 1

Coals from Old Database Tested for Fly Ash Tensile Strength

Run #	Coal Name	Symbol	Source	Rank	Inlet Dust Loading, grains/scf	Baghouse Particulate Removal Efficiency, %	Particulate Penetration, %
253	Big Brown	BB2	Freestone Co., TX	Lignite	6.4	83.5	16.5
263	Phillips "A"	PA	Panola Co., TX	Lignite	5.3	86.3	13.7
237	Choctaw (washed)	CW	Choctaw Co., AL	Lignite	2.7	89.6	10.4
246	Naughton	NT	Lincoln Co., WY	Subbit.	1.6	93.6	6.4
273	Falkirk	FK	McLean Co., ND	Lignite	4.0	94.7	5.3
245	Arapahoe	AR	Routt Co., CO	Subbit.	2.8	95.5	4.5
250	Antelope High Na	AN max	Wyoming	Subbit.	1.5	99.1	0.9
267	Velva	V5	McLean Co., ND	Lignite	2.5	99.4	0.6
268	Sarpy Creek	SC	Big Horn Co., MT	Subbit.	3.5	99.65	0.35
270	Wyodak	WD	Cambell Co., WY	Subbit.	2.4	99.69	0.31
247	Indian Head	I3	Mercer Co., ND	Lignite	2.5	99.7	0.3
249	Antelope/Spring Creek	AN/SP	Wyoming	Subbit.	1.6	99.8	0.2
244	Velva	V4	McLean Co., ND	Lignite	2.0	99.8	0.2
216	Beulah High Na	BA	Mercer Co., ND	Lignite	2.1	99.8	0.2

Figure 6. Cohesive tensile strength as a function of ash porosity for pulverized coal-fired ashes from pilot-scale shaker baghouse tests.

Figure 7. Cohesive tensile strength as a function of ash porosity for pulverized coal-fired ashes from pilot-scale shaker baghouse tests.

Figure 8. Correlation between baghouse particulate penetration and tensile strength.

included in the correlation, the lowest tensile strengths still correlate well with the highest emissions and the highest tensile strengths correlate with the lowest emissions. These new data provide further evidence that tensile strength can be used to predict emissions from a fabric filter. In proceeding with a more general model, the challenge then is to successfully incorporate tensile strength along with pore size, particle size, velocity, cleaning methods, and cleaning frequency.

Correlation Between Fabric Filter Pressure Drop and Packed Porosity

Assuming viscous flow, pressure drop across a fabric filter is given as:

$$\Delta P = K_f V + K_2 W_R V + K_2 C V^2 t / 7000 \quad [\text{Eq. 1}]$$

where

- ΔP = differential pressure across the baghouse tube sheet (in. of water)
- K_f = fabric/dust resistance coefficient (in. of water-min/ft)
- V = face velocity or air-to-cloth ratio (ft/min)
- K_2 = specific dust cake resistance coefficient (in. of water-ft-min/lb)
- W_R = residual dust cake weight (lb/ft²)
- C = dust loading (grains/scf)
- t = filtration time between bag cleanings (min)

The first term in Equation 1 accounts for the pressure drop across the fabric. For a new fabric, pressure drop across the fabric alone is generally negligible, but in cases where the dust packs permanently into the interstitial spaces of the fabric, this may be a significant term. The second term in Equation 1 accounts for the pressure drop contribution from the permanent residual dust cake that exists on the surface of the fabric. In many cases, after long-term operation, this is a significant term. The third term in Equation 1 accounts for the pressure drop contribution from the dust accumulated on the bags since the last bag cleaning. K_2 is determined primarily by the fly ash particle-size distribution and the porosity of the dust cake. For accurate prediction of pressure drop, the primary challenge is to predict both K_2 and W_R . As previously stated, both the residual dust cake weight and the porosity of the dust cake will depend on cohesive dust properties. This means that both can probably be predicted from quantitative measurements such as tensile strength or porosity. K_2 values can be reported as an initial value and as the effective value. The initial value is based on the linear part of the ΔP versus time curve from the first filtration cycle, starting with new bags. During the first filtration cycle, the ΔP contribution from the first term is negligible, and there is no residual dust cake, so K_2 can be readily obtained from the third term in Equation 1. An effective K_2 value is based on a ΔP that is an average of the difference between the before- and after-cleaning ΔP s. Effective K_2 is higher than the initial K_2 because the bags generally do not clean uniformly, and some of the dust is dispersed and redeposited on the bags after on-line pulsing. Therefore, effective K_2 includes cake release and redispersion in addition to particle size and porosity. The correlations shown in Figure 9 for the 100-hour pulse-jet tests indicate that both initial and effective K_2 can be predicted by the packed porosity of the fly ash. The data are from tests with Ryton fabric at A/C ratios of 4 and 6 ft/min with three different coals. These correlations likely would not be valid, however, if the particle-size distributions varied significantly.

The more complex dependence of K_2 on face velocity and particle size in addition to cohesive properties is shown in Figure 10, which presents K_2 data from bench-scale pore-bridging experiments. The K_2 dependence on velocity is much less significant for the more cohesive conditioned samples than for the baseline samples. The 4.5- μm -mass-median-diameter (MMD) dusts had higher K_2 values, as expected. Pressure drop models, such as Carman-Kozeny, exhibit an inverse-square relationship between K_2 and particle size, which indicates that K_2 for a 4.5- μm dust would be approximately 8 times greater than the K_2 for a 13- μm dust at constant porosity. Typically, a smaller particle size forms a more porous cake, partially offsetting the particle-size effect. Thus the K_2 values of the 4.5- μm dusts were only from 1.2 to 2.5 times greater than the K_2 values of the 13- μm dusts. In addition, MMD values generally cannot be used in the theoretical Carman-Kozeny model, which is based on monosized particles. For fabric filters with a narrow range in face velocity and filtering dusts of similar particle-size distributions, it appears that packed porosity measurements are good predictors of K_2 , as indicated by Figure 9. A more general predictive model for K_2 , however, must include particle size and face velocity in addition to packed porosity.

Summary and Discussion of Preliminary Modeling Efforts

Tensile strength, aerated porosity, and packed porosity measurements are appropriate methods to quantify the cohesive properties of fly ash. Fly ashes with tensile strengths of less than 50 N/m² are likely to have significantly greater ESP rapping dispersion of fine particles than fly ashes with tensile strengths greater than 250 N/m². Fly ash tensile strength also appears to be a good predictor of fabric filter particulate

Figure 9. Initial and effective K_2 as a function of packed porosity for 100-hour pulse-jet tests with Ryton fabric at A/C ratios of 4 and 6 ft/min.

Figure 10. Effect of face velocity on K_2 for screen tests with baseline and conditioned Monticello fly ash.

emissions. Fine-particle emissions from a pulse-jet baghouse with Ryton felted fabric were 100 times greater for a fly ash with a tensile strength less than 100 N/m^2 compared to fly ashes with tensile strengths greater than 250 N/m^2 . High emissions from a shaker-cleaned woven glass fabric also correlated with low tensile strength. In direct pore-bridging experiments with monosized openings, tensile strength was found to be an indicator of maximum bridging velocity, which is an independent indicator of emissions with a variable face velocity. Therefore, tensile strength is an important dust characteristic that can be used as a basis to model fabric filter emissions. The bench-scale pore-bridging tests also prove that face velocity must be included in the model. Beyond these, the most important parameter is the fabric itself, which in the extreme cases, will be the controlling factor determining emissions. For example, if a microporous fabric were available such that the average pore size in the fabric was smaller than the dust particle size, 100% collection efficiency would be attained independent of the tensile strength and velocity. Similarly, a filter with very large openings might never attain a

high collection efficiency, even with a low velocity and a high tensile strength dust. However, within the range of fabrics commonly used in baghouses, tensile strength and face velocity are perhaps the two most important parameters that will determine collection efficiency. The fabric effect is difficult to quantify because of the complexity of weaves, felts, yarns, fibers, and finishes that are available. If each fabric could be represented by a single average pore size, incorporating the fabric effect into a general model would be more straightforward. Until that is demonstrated, emission models will likely be limited to a single fabric at a time. Therefore, a key research need is to explore whether fabrics might be reasonably represented by a single average pore size. Other dust properties, such as particle size and porosity, and bag cleaning parameters, such as cleaning method, cleaning energy, and cleaning frequency, will also need to be included in a more comprehensive model.

In tests with pulse jet-cleaned Ryton bags, packed porosity was a good indicator of initial or effective K_2 . Bench-scale tests, however, indicate that particle size and face velocity must also be incorporated into a model to predict pressure drop as a function of dust properties.

Tensile Strength of PFBC Fly Ash

Fly ash samples from the Tidd and Karhula PFBC facilities were sent to the EERC from METC to measure the tensile strength. Significant filter-cleaning problems have occurred at the Tidd plant, while filter cleaning has not been as serious at the Karhula plant. Reasons for the differences are likely related to the cohesive characteristics of the ash. The tensile strength versus porosity curves for these ashes are shown in Figure 11 along with the tensile strength of an AFBC fly ash sample from the Shawnee plant that we previously measured. Tensile strengths of fly ashes from pulverized coal firing of Blacksville Pittsburgh No. 8 bituminous and Absaloka subbituminous coals from recent tests are also shown in Figure 11. Comparing the Tidd and Karhula samples, the Tidd fly ash clearly has a much higher tensile strength, which is consistent with the filter-cleaning problems that have been observed. However, the tensile strength measurements are completed at room temperature after storing the fly ash at 10% relative humidity for at least 24 hours. Whether these measurements are indicative of the tensile strengths at the hot filtration temperatures in a PFBC is unknown. If sintering of the dust cake or other chemical changes occur while the fly ash resides on the ceramic filters, tensile strength measurements conducted after cooling the ash may be irrelevant. On the other hand, if the dust cake strength is primarily the result of the relatively weak particle-particle binding forces that are typical of bulk powders, then tensile strength measurements may indeed be an indicator of dust cake strength. The different tensile strength between the Tidd and Karhula fly ashes may be the result of differences in fly ash chemistry, morphology, and particle size. The particle size of the Karhula ash was fairly large (22.0 μm volumetric median diameter [VMD]), while the Tidd ash was small (3.0 μm VMD). The differences in particle size alone are likely to yield different dust cake properties. For the same material, the finer particle size will have the greater tensile strength. Whether the large difference in tensile strength for the two PFBC ashes is the result of differences in particle size alone is unknown. The VMD of the AFBC ash was 5.5 μm and the VMDs of the Blacksville and Absaloka ashes were in the range from 12 to 15 μm . The tensile strengths for the Blacksville and Absaloka ashes are clearly different, but the particle size was similar. In this case, the tensile strength differences are attributed to differences in ash chemistry and/or particle morphology. The maximum

Figure 11. Comparison of tensile strength versus ash porosity curves for Blacksville and Absaloka pulverized coal-fired ashes, Shawnee AFBC ash, and Tidd and Karhula PFBC ashes.

tensile strengths measured for the Blacksville and Absaloka ashes were 200–300 N/m², which based on the correlation between tensile strength and particulate emissions, predicts that these ashes should be easy to collect in a fabric filter. Actual particulate emissions from a pulse-jet fabric filter with Ryton felted bags were very low, which again verifies the correlation.

Bench-Scale Pore-Bridging and Reentrainment Experiments

Last year, the EERC conducted tests with a horizontal reentrainment test system (flow parallel to the ash surface) to determine the threshold velocities at which reentrainment would occur (23). Objectives of the horizontal reentrainment tests were to determine the velocity at which reentrainment occurs and to relate reentrainment velocity to the cohesive properties of the ash. The reentrainment velocity should depend on the particle–particle binding forces which can be approximated as follows. Measured tensile strengths of baseline and conditioned fly ash with a MMD of about 13 μ m have ranged from 10 N/m² to 2000 N/m². Assuming monosized 13- μ m spherical particles and simple cubic packing (corresponding to a porosity of 47.6%), 590,000 particles would be in contact in an area of 1 cm². This corresponds to an average particle–particle binding force of 1.7×10^{-8} N for a dust with a tensile strength of 10 N/m². The actual particle–particle binding force will likely be somewhat higher because the porosity is typically greater than 47.6% and the pore structure will not result in a perfect packing arrangement. The particle–particle binding forces must be overcome by a fluid drag force for particle reentrainment to occur. Applying Stokes' law, the velocity at which the drag force is equivalent to a 1.7×10^{-8} N particle–particle binding force is 25 ft/sec for a 13- μ m

spherical particle. This velocity is within the range of velocities for which significant reentrainment was observed. The actual conditions at the boundary layer, where the reentrainment occurred, are unknown; however, the Reynolds numbers for flow through the flow gate in the horizontal reentrainment test system were well within the turbulent flow region. The most significant reentrainment occurred somewhat downstream from the gate and may have been influenced by turbulent eddies. Although a laminar sublayer may exist at the dust surface, calculation of the exact drag force on the particles that were reentrained is difficult because the exact location where the particles were initially at rest (relative to the gate orientation) is unknown and turbulent conditions were present. Nevertheless, the results indicate that fairly high velocities are necessary to produce a Stokes' drag velocity of 25 ft/sec in order to overcome a particle-particle binding force of 1.7×10^{-8} N.

Velocities in the range of 5 to 25 ft/sec are 75 to 375 times greater than the common filtration face velocity of 4 ft/min used with pulse-jet baghouses. For a dust cake porosity of 50%, the actual velocity of the gas through the cake would be twice as great, which is still 37 times less than the minimum velocity at which reentrainment occurred. This implies that particle reentrainment due to viscous drag within the bulk of a dust cake should not occur under normal filtration conditions since the velocities are too low. On the other hand, if velocities are greater than 5 ft/sec, particle reentrainment is expected. Local velocities can greatly exceed 5 ft/sec when pinholes develop in the dust cake. From capillary flow calculations, the velocity through a 100- μ m-diameter pinhole can be 100 to 1000 times greater than the face velocity, or 400 to 4000 ft/min (6.7 to 67 ft/sec) for a typical face velocity of 4 ft/min. 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 bridged quickly for high particulate-removal efficiency. Therefore, dusts with superior pore-bridging ability will obviously be collected with higher efficiencies, and if pore-bridging ability (or resistance to reentrainment) can be predicted from cohesive measurements, then collection efficiency can also be predicted from these measurements.

Since the horizontal reentrainment tests indicated reentrainment would occur only at much higher velocities than are typically found in conventional filtration (except in pinholes), a different type of reentrainment experiment was conducted this year. The procedure involved the use of the electroformed sieves that were used in the previous pore-bridging experiments. However, ash was fed for only a short interval at a velocity of 2 ft/min so that dust accumulated only along the edges of the openings in the screens. During this interval, particulate emissions were high because bridging of the openings had not occurred yet. The dust feed was then stopped and the velocity reduced to 1 ft/min while particulate emissions decreased to background levels. The velocity was then increased back to 2 ft/min, which typically resulted in only a slight increase in emissions. Then the velocity was increased to 4, 8, and 16 ft/min while emissions were monitored. Results from these tests, shown in Figures 12-22, indicate that significant reentrainment spikes occur when the velocity is increased beyond 2 ft/min. This reentrainment occurs at velocities far below the 5-ft/sec (300-ft/min) threshold reentrainment velocity seen with the horizontal reentrainment test system. Since the reentrainment must occur as a result of fluid drag overcoming particle-particle binding forces and the particle-particle binding forces are expected to be similar, the reentrainment geometry must be different. To bridge the 150- μ m openings in the screen, 10 to 15 particle layers are required.

Therefore, the particle deposit structure prior to bridging must consist of long chains of particles that are loosely attached to the edges of the screen openings. These structures protruding from the screen edges evidently can be reentrained at much lower velocities than individual particles.

One of the variables of interest is the relationship between the length of time of initial dust feed and the level of emissions. Similar reentrainment tests were conducted with initial ash feed times ranging from 2.5 to 20 minutes. At 20 minutes, complete pore bridging still had not occurred. Results from a series of these tests, shown in Figures 19 and 20 indicate that the concentrations of the reentrainment spikes at 4, 8, and 16 ft/min were somewhat affected by the initial feed time but perhaps not to the extent expected. Velocity, however, appears to be the most critical parameter affecting the level of reentrainment. In general, the reentrainment at 2 ft/min was just detectable above the background. This is not surprising since the particles were initially collected at a face velocity of 2 ft/min. If the particles were retained at that velocity during initial collection, they would not be expected to reentrain after the velocity was reduced to 1 ft/min and then increased again to 2 ft/min. However, when the velocity was increased to 4 ft/min, noticeable reentrainment occurred over the entire range of initial ash feed times. When the velocity was increased to 8 ft/min, the reentrainment spike was 10 times greater than at 4 ft/min. This reentrainment is in addition to the reentrainment at 4 ft/min, since the tests were conducted in sequence without additional ash feed between the increases in velocity. At 16 ft/min, the reentrainment spike was about the same as at 8 ft/min, but this also represents additional reentrainment that did not occur at 8 ft/min.

Figure 12. Particle reentrainment from a 150- μ m screen measured with a condensation particle counter with an initial ash feed time of 2.5 min.

Figure 13. Particle reentrainment from a 150- μ m screen measured with a condensation particle counter with an initial ash feed time of 5 min.

Figure 14. Particle reentrainment from a 150- μ m screen measured with a condensation particle counter with an initial ash feed time of 7.5 min.

Figure 15. Particle reentrainment from a 150- μ m screen measured with a condensation particle counter with an initial ash feed time of 10 min.

Figure 16. Particle reentrainment from a 150- μ m screen measured with a condensation particle counter with an initial ash feed time of 12.5 min.

Figure 17. Particle reentrainment from a 150- μ m screen measured with a condensation particle counter with an initial ash feed time of 15 min.

Figure 18. Particle reentrainment from a 150- μ m screen measured with a condensation particle counter with an initial ash feed time of 20 min.

Figure 19. Summary of peak reentrainment concentration measured with a condensation particle counter as a function of initial ash feed time for conditioned Monticello fly ash and a 150- μ m screen.

Figure 20. Summary of peak reentrainment concentration measured with a condensation particle counter as a function of initial ash feed time for baseline (unconditioned) Monticello fly ash and a 150- μ m screen.

Figure 21. Particle reentrainment from a 75- μ m screen measured with a condensation particle counter with an initial ash feed time of 2.5 min.

Figure 22. Particle reentrainment from a 75- μ m screen measured with a condensation particle counter with an initial ash feed time of 12 min.

Figures 21 and 22 indicate that similar levels of reentrainment were seen when the screen size was reduced to 75 μm . Evidently, multiple particle chains are still formed during the initial bridging process, and these structures are very susceptible to reentrainment.

Color photographs were taken at 5-min intervals while dust was fed continuously at a velocity of 2 ft/min in an attempt to determine the nature of the reentrainment that occurred. The photographs showed that the particles initially form chainlike structures that eventually meet to form bridges over the 150- μm openings. These photographs were not included in this report because resolution was reduced when black and white photographs were made from the color negatives. However, one of the mechanisms of reentrainment apparent from the color photographs is the breaking loose and reentrainment of an entire bridge.

Further tests were conducted with an initial dust feed time of less than 5 min to determine the type of structure that is reentrained with increases in velocity before pores are bridged. Close examination of deposit photographs before each increase in velocity revealed that larger particles can be reentrained individually at higher velocities; however, the limit of resolution was reached so that the structure of small individual particles or chains that were reentrained at a given velocity could not be determined.

These tests indicate that face velocity is one of the most important parameters affecting pore-bridging ability and reentrainment potential. Further modeling efforts to relate emissions to cohesive properties must also incorporate velocity. The general trend that was demonstrated in Figure 3, showing the strong dependence of emissions on tensile strength, is likely to hold true over a range of face velocities. However, the data suggest that at higher velocities, a much greater tensile strength may be required to achieve the same level of fine particulate collection efficiency that can be achieved at lower velocities. Therefore, a model that can adequately predict emissions from both tensile strength and velocity data is needed. A significant amount of additional research effort will be required to develop such a working model.

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Advanced Power Systems
Task 3.0

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EXECUTIVE SUMMARY

INTRODUCTION

One of the overall goals of the U.S. Department of Energy (DOE) is the development of technology necessary to provide for secure, reliable, affordable, and environmentally sound sources of energy. This is important because of the need to ensure economic stability and growth in the next century as well as the need to reduce current and minimize future environmental impacts associated with power generation in the United States and in the world as a whole. The continued and potentially expanded use of abundant coal reserves is one key to a secure and affordable source of energy.

Throughout the world, coal will play an expanded role in the production of affordable energy necessary to meet the demands of economic development and growth. The development of more efficient and environmentally sound technology in the United States may present export market opportunities throughout the world. Specific examples include East Central Europe and the Pacific Rim. In East Central Europe, where substantial coal use has continued for decades, an urgent need exists for commercial emissions control technology as well as for clean coal technology currently being developed. The lack of emission control technology in East Central Europe is exacting a high price in terms of human health and long-term environmental damage. In contrast, the Pacific Rim has only recently begun to expand the use of coal to meet energy demands motivated by economic growth. Therefore, the need in the Pacific Rim is for commercial and developing technologies for new coal-fired plants to meet current and future energy demands in an environmentally sound manner.

In order for to continue coal to play a key role in the U.S. energy mix, it will be necessary to develop and commercialize technologies capable of producing electricity at significantly higher overall system efficiencies than the 25%-35% levels currently observed in conventional coal-fired systems. Also, the production of liquid and gaseous fuels from coal will be necessary in order to effectively meet the broad spectrum of future energy needs. In order to achieve overall system efficiencies of 40%-60% in an environmentally acceptable manner, development and demonstration of advanced second-generation utilization and conversion technology will be necessary. Examples include 1) advanced pulverized coal-fired combustion systems, 2) high-temperature heat exchangers for indirect firing of gas turbines; 3) pressurized combustion in staged, entrained, slagging, and fluidized-bed modes; 4) integrated gasification and direct gas-fired turbines; and 5) close-coupled integration of catalytic gasification with fuel cells.

A number of barrier issues exist that are not unique to individual technologies, but are in some manner common to all advanced power system processes for both oxidizing and reducing environments. Examples include 1) the impact of coal ash constituents, specifically alkali components; 2) hot-gas cleanup (fly ash, sulfur, and nitrogen oxides); 3) materials issues, specifically ceramic and refractory components; and 4) operational issues unique to high-temperature pressurized systems.

The long-term objective of the Advanced Power Systems program area is to address current and yet-to-be-identified barrier issues to the commercialization of second-generation advanced power technologies. The general approach will be to expand the

current fundamental knowledge base that has evolved from the conventional utilization of coal and use the expanded knowledge base to either tailor the fuel form to the utilization process or to modify the utilization process to compensate for adverse fuel properties. Four key task areas have been identified for the Advanced Power Systems program: 1) fuel utilization properties, 2) pressurized combustion, 3) catalytic gasification, and 4) hot-gas cleaning. Accomplishments for the project year January through December 1993 are summarized in the following paragraphs.

ACCOMPLISHMENTS

Fuel Utilization Properties

The overall goal of the Fuel Utilization Properties (FUP) task is to determine the fundamental physical and chemical transformations of coal inorganic constituents and the relationship of the resulting ash intermediates to the formation of ash deposits in advanced power systems. Combustion tests were performed under standard and fuel-rich conditions on Wyodak, Beulah, Upper Freeport, and Black Thunder coals. The Black Thunder coal was selected for ash transformation studies to be performed in collaboration with another DOE project being coordinated by Physical Sciences Incorporated (PSI). The effects of low- NO_x conditions on ash transformations were extrapolated from the fuel-rich combustion tests performed on Black Thunder and Illinois No. 6 coals.

For the Black Thunder ash, the effect of fuel-rich conditions appeared to be an increase in quartz, calcite, dolomite, and calcium-rich phases, along with a decrease in calcium-aluminosilicate phases. This may have been the effect of the lower particle temperature and oxygen-lean atmosphere reducing the interaction and assimilation of pure quartz and organically-bound calcium. The Black Thunder fly ash produced under full air conditions is dominated by particles rich in calcium-aluminosilicate material. For the Illinois No. 6 ash, the fuel-rich conditions give a decrease in iron oxide, iron-aluminosilicates, mixed aluminosilicates, and iron silicate. There is a corresponding increase in iron sulfide and carbonate. The fuel-rich conditions appear to prevent the oxidation of pyrite and pyrrhotite to iron oxide, as well as decreasing assimilation of iron into aluminosilicate phases caused by the lower temperatures.

The model ATRAN, which has been developed at the EERC for use as a research tool in predicting fly ash particle size and composition, has undergone significant advances in the last year. The FORTRAN version of the code was updated with a user friendly graphical interface for easier use by researchers. The interface provides for convenient input of data and viewing of the results. In addition to the FORTRAN version, ATRAN was ported and recoded into powerful C language. The new C version, which does not yet contain a user-friendly interface, is designed as a module for easy incorporation into other models. The application of this model to advanced coal conversion processes can be done by adding reduced mineral species information.

A first-phase round-robin study between seven laboratories to evaluate the CCSEM method of quantitative coal mineral analysis is nearly completed. Five laboratories have analyzed the Pittsburgh No. 8 coal, and three laboratories have analyzed the Illinois No. 6 and Prince coals. A statistical analysis of the results will be performed when all the results have been obtained.

The particle-by-particle scanning electron microscopy (PBPSEM) method that was developed to size, identify, and quantify coal minerals and their degree of association with the organic matrix was further developed and assessed for its future applicability. The quantitative mineralogy results compare favorably with a normal CCSEM analysis, whereas the particle-size and image analysis results do not. Some of the variation is attributable to large differences in the sample populations. The main weaknesses of PBPSEM technique are that it requires too much time to run one sample and it still lacks accuracy for particles that are less than 3 μm in diameter.

In the area of combustion testing for the development of ash formation and ash deposition algorithms, a literature search was conducted covering the topics of ash transport, deposit initiation, ash deposition, and silicate and sulfate sintering behavior. A fourth high-temperature furnace has been installed on the optical access drop-tube furnace (ODTF). This allows longer particle residence times and higher particle velocities. At the same time, several other minor modifications and improvements were made to the ODTF. A prototype of the convective pass simulator (CPS) for the ODTF has been fabricated. The purpose of the CPS is to trap and remove the larger particulate material in the high-temperature region of the furnace, while allowing finer particulate material to continue on and impact the deposition probe. This will more closely simulate the conditions in the convective pass of a utility boiler. Work was completed on investigating the key factors in ash deposit initiation during pulverized coal combustion. Work was also performed to establish the key factors involved in deposit strength development. The strength of the deposit itself was shown to be related to the deposit composition, the deposit temperature, and the deposit time-temperature history. First order algorithms were devised that generally describe ash transport, deposition, and strength development. Plans were made to continue studying the effects of ash optical and thermal conductivity properties on heat transfer, with the aid of Dr. Terry Wall from the University of Newcastle.

The role of viscosity of liquid phases in deposits will be further investigated through the work of a doctoral candidate who was being supported through this project. Mr. Bruce Folkedahl began a doctoral research program at Pennsylvania State University to focus on the development of a more effective slag viscosity model for higher-calcium coals such as the western U.S. types.

Pressurized Combustion

The goal of the pressurized fluidized-bed combustion (PFBC) activity is to generate fundamental process information that will further the development of an economical and environmentally acceptable second-generation PFBC. The immediate objectives focus on generic issues including the fate of alkali, the sulfide species in the carbonizer char, and the RCRA heavy metals in PFBC. A great deal of PFBC performance relates to the chemistry of the bed and the gas-solids contacting that occurs during combustion. These factors can be studied in a suitably designed bench-scale reactor. Future studies will focus on the emission control strategies applying in the bed rather than in hot-gas cleaning. Emissions include alkali and heavy metals in addition to SO_2 , NO_x , N_2O , and CO. The objective of slag attack research is to mitigate slag corrosion of ceramic materials in a slagging coal-fired combustor.

Construction and shakedown of the pressurized fluidized-bed reactor was completed, and parametric testing of alkali getter effectiveness is underway. A second

test matrix is being developed with Foster Wheeler Development Corporation to evaluate products of carbonizer char combustion. Funding limitations have necessitated the postponement of the heavy metals activities outlined in the initial statement of work.

To obtain higher efficiencies in coal-fired power systems, higher temperatures of the working fluid within a heat exchanger are required. Several candidate alloys or ceramics are available that will provide structural stability and chemical stability in air, although ceramics will be required for temperatures over about 980°C. Silicon carbide-based structural ceramics are targeted for the higher temperatures because of their high thermal conductivities and high strengths. Theoretically, they should be stable to around 1425°C in a combustion environment. However, tests performed at the EERC under another project have shown that dense SiC is prone to slow, but unacceptable, corrosion by ash at temperatures above about 1200°C. Therefore, protective high-conductivity coatings such as SiC-based refractories are needed to prevent corrosion of the ceramic surface by coal slag. However, the corrosion resistance of the refractories was not known. During this year corrosion resistance measurements were made using commercially available refractories. The focus has been on monolithic refractories because compared to brick refractories they are much cheaper, can be easily installed and replaced in the field, and maintain intimate contact with the heat exchanger so that heat transfer is as high as possible. The tests showed that commercially available monolithic refractories were useable only to approximately 1200°C in a slagging environment. Above that temperature, the binder materials rapidly dissolve in the slag.

In order to increase monolithic refractory operating temperatures, methods of decreasing the corrosivity of the slag were investigated. They included testing additives that would make the slag less corrosive and developing new refractory binders. This testing was performed in conjunction with that done for the DOE Combustion 2000 project. Additives were found to crystallize out iron from the slag, making it less likely to actively corrode the SiC in the refractories. Other additives were used to increase the solidus temperature of the slag to above 1400°C. If added with the coal feed to a slagging system, the additives would freeze a layer of slag next to the refractory, thereby reducing its corrosion rate. Also, a new binder was developed in the Combustion 2000 research that is 10 times more resistant to high-iron slag penetration than commercially available materials. Finally, a new binder was developed that is a hydraulic cement yet fires into a strong high-temperature matrix that helps to solidify Powder River Basin slag into which it has partially dissolved, with the aim of rendering the slag noncorrosive. This latest work showed promise, but was nonconclusive since time and funding were depleted.

Catalytic Gasification

Work on catalytic gasification was in direct support of efforts to integrate gasification and molten carbonate fuel cells. The primary goal was to identify a suitable gasification catalyst to achieve coal residence times on the order of minutes in a gasifier operating on naturally reactive low-rank coal at nominal conditions of 650°C and 500 psi. A second objective involved integrating the EERC gasification model into existing state-of-the-art codes.

Catalytic gasification coupled with a molten carbonate fuel cell offers an extremely efficient and environmentally sound power generating system using coal. An ideal process would be one in which a suitable hydrogasification catalyst was found which

would allow for residence times on the order of minutes at 650°C and 500 psi. Work with an Illinois No. 6 bituminous coal has shown that low reaction rates for bituminous coal, even when catalyzed with the best catalysts known to date, preclude their consideration as a feedstock for an integrated gasification-molten carbonate fuel cell plant. In contrast, a lignite was shown to have a 10-35 times higher catalyzed char-steam gasification rate than the bituminous coal at ambient pressure. Both produced methane during pyrolysis, but the lignite, with the aid of catalysts, was able to sustain a methane production during hydrogasification while the bituminous coal was not. Further enhancement of methane production can be accomplished by carrying out the reaction at increased pressure.

Both nickel and iron catalysts were successful in increasing methane production but the iron seemed to be more effective during both pyrolysis and hydrogasification phases of the gasification. On-line tracking of the gases with Fourier transform infrared (FT-IR) spectrometry provides a highly satisfactory monitoring tool for the progress of the process during gasification.

Iron-calcium catalyst not only increased methane production, but also increased the rate of lignite char-steam reaction over that of the Fe-catalyzed gasification. The Fe catalysts show great promise for promoting a gasification product gas stream suitable for fuel cell feed.

A computer program was developed to calculate equilibrium gas compositions for the gasification of coal by steam, oxygen, and/or hydrogen. The solution satisfies the combined equilibrium conditions for steam gasification, water-gas shift reaction, methanation, and the enthalpy balance. The menu-driven program, written in Quick Basic®, has been integrated with a Lotus 123® spreadsheet. An additional Lotus spreadsheet, for enthalpy calculations alone, has a built-in capability for minimizing errors in the heat and material balance for a coal conversion system with up to 4 input streams and 2 output streams. These programs have shown quite good agreement with experimental data from the literature for a range of gasification conditions and for predicting coal higher heating values.

Hot-Gas Cleaning

The overall objective of the hot-gas cleanup task is to develop reliable methods of removing particulate matter from high-temperature and high-pressure gas streams produced from coal combustion or gasification. The primary area of research to date has involved determinations of rates and mechanisms of alkali corrosion of ceramic filter materials. The research has focused on reactions occurring at approximately 980°C in an oxidizing environment.

The key to successful ash removal is an understanding of the properties of the ash to be collected as well as the interactions of this material with the barrier itself. The knowledge base under development will assist in assessing many of these barrier material issues for a variety of coal ashes. A variety of strategies have been considered to mitigate problems related to corrosion and blinding of filters by the products of coal combustion. They include coating the filters with corrosion resistant materials, developing computer codes to help design mitigation strategies, and removing some of the corrosive species from the gas stream.

Two methods were developed for coating silicon carbide (SiC) with tantalum pentoxide. Tantalum pentoxide has been shown to prevent corrosion of SiC by alkali salts at temperatures of 1000°C and so may protect SiC candle filters from corrosion by alkali vapors. The coating methods involve electron beam deposition followed by anodization. In addition, a reactor was built that will be used to test ash sintering and corrosion of candle filter rings. During 1994, 1-in. wide rings of candle filter materials will be bolted together and coated with ash; alkali vapor-laden simulated flue gas will be passed through them for up to 500 hours to determine the rates and mechanisms of ash cake formation, blinding, sintering, and corrosion of the filters. Strength loss will be determined by C-ring compression tests at temperature.

A computer model that can be used to determine the most efficient types and concentrations of alkali getters was modified to expand its database and make it easier to use. The model is termed TEACH for "thermochemical equilibrium analysis of coals and ashes." It replaces the earlier thermochemical equilibrium computer model named PHOEBE. The database for TEACH has been expanded to 6000 species, and now operates on specific heat rather than Gibb's free energy data. In addition, the user interface has been greatly simplified to allow modeling of interactions between coal ash, coal additives, and additive concentrations to be performed in large batches rather than singly. This permits easy setup of large test matrices that can be run during nonbusiness hours. TEACH was used to model equilibrium concentrations of all sodium species in the gas phase of a combustor burning a high-sodium coal and turn the data into a three-dimensional graph showing sodium vapor versus temperature versus amount of getter material. The graph shows that at just under 1500°C, the temperature used in earlier gettering experimental work, approximately one-half of the vapor-phase sodium species can be gettered by the addition of kaolin at a ratio of kaolin to ash of 0.5. This is approximately the same as that measured in experimental tests, showing that simple mixing of the kaolin with coal is sufficient to provide the maximum possible equilibrium absorption of sodium species at high temperatures. The graph shows that at lower temperatures and with greater levels of kaolin addition, less sodium is present at equilibrium (which may not be achieved before hot-gas cleaning) in the vapor phase. At 1000°C and with no kaolin added, a situation such as that near a hot-gas cleanup device in a system burning this coal, approximately 50 parts per billion by mass (ppbm) sodium species are at equilibrium in the gas phase, primarily as sodium hydroxide and sodium sulfate. This is double what is presently permitted by some high-efficiency turbine manufacturers for the inlet to the turbine. However, at a kaolin addition rate of one-half of the ASTM ash rate, the vapor-phase sodium species drop to 13 ppbm at 1000°C. Concentrations remain at about this level all the way to 1300°C when kaolin is added at the same rate as the ASTM ash.

In addition to the modeling work, a detailed literature search was completed on the information available for incorporation into a knowledge base of materials information. The knowledge base concept is proposed as the future for materials modeling. It would consist of a large database of experimental information relevant to materials and an algorithm library for manipulating that data. Such a knowledgebase would be used to predict the interactions of coal combustion products with structural and refractory ceramic materials in advanced energy systems.

TASK 3.0 ADVANCED POWER SYSTEMS

Subtask 3.1 Fuel Utilization Properties

INTRODUCTION

The mission of the U.S. Department of Energy (DOE) and the Energy & Environmental Research Center (EERC) Cooperative Agreement is to promote the clean and efficient use of energy resources through a program of research and development efforts. These efforts include research characterization, air quality impacts and controls, advanced power systems, and advanced fuel forms. The goals of the Cooperative Agreement are energy efficiency, preserving the environment, securing the domestic energy supply, diversifying the coal industry, and fortifying foundations in research, education, and technology commercialization.

OBJECTIVES

This report covers the activities of Subtask 3.1, Fuel Utilization Properties. The overall goal is to determine the fundamental physical and chemical transformations of coal inorganic constituents and the relationship of the resulting ash intermediates to the formation of ash deposits in low-NO_x combustion and advanced power systems. In the context of this project, "advanced coal conversion" refers to fuel-rich combustion, pressurized combustion, fuel-rich pressurized combustion, gasification, and advanced coal conversion conditions similar to those found in the private sector.

The overall objectives of Subtask 3.1 are 1) to determine the mechanisms of inorganic transformations during coal conversion processes, 2) to develop algorithms to predict the transport mechanisms of an ash-particulate flux to heat-transfer surfaces, 3) to study the effect of deposit characteristics on deposit strength and heat-transfer properties, and 4) to examine the effects of deposit characteristics on deposit removability. The following details the objectives of each constituent task for the past year of work.

Inorganic Transformations and Production of Ash Intermediates

There are three objectives:

- Perform inorganic transformation studies on three coals using standard combustion and fuel-rich combustion.
- Refine the stochastic ATRAN model for fly ash composition and size prediction and investigate its application to advanced coal conversion systems.
- Develop and assess the particle-by-particle scanning electron microscopy (PBPSEM) method and standardize the computer-controlled scanning electron microscopy (CCSEM) method through round-robin collaborative testing.

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Ash Transport and Deposit Initiation and Growth

There are five objectives:

- Perform a literature review in the area of ash transport and deposit initiation.
- Perform modifications of the optical drop-tube furnace (ODTF) to add a second furnace for generating longer particle residence times and greater particle velocities, develop a convective pass simulator for the ODTF, and install additional computer control and image analysis capabilities.
- Perform deposit initiation studies.
- Develop first-order transport algorithms to determine sticking fractions of entrained particulates.
- Study deposit growth rates for fouling and slagging deposits.

Deposit Strength Development, Thermal Properties, and Removability

There are five objectives:

- Conduct a literature review in the area of the principles of silicate and sulfate sintering and in the area of deposit thermal conductivity.
- Perform sintering and deposit thermal conductivity experiments.
- Develop a first-order correlation between deposit porosity, composition, degree of sulfonation, and liquid-phase viscosity with deposit growth rates, strength development, and removability.
- Develop a more effective slag viscosity model (conducted as a doctoral research project at Pennsylvania State University).

ACCOMPLISHMENTS

Inorganic Transformations and Production of Ash Intermediates

The first-year goals were to 1) perform inorganic transformation studies on coals under standard combustion conditions, 2) refine the stochastic ATRAN model for fly ash composition and size prediction, and 3) evaluate the particle-by-particle CCSEM method and develop standardization of the CCSEM method through round-robin collaborative testing.

Black Thunder Coal Sample Distribution

The EERC prepared and distributed representative samples of pulverized Black Thunder coal to members of the PSIT working group as part of the Fuels Utilization

Properties (FUP) project to allow all members to study a common coal sample. The coal was crushed, representatively split, pulverized, and distributed to the members of the working group. An additional amount of the pulverized coal was retained as a reserve sample for future use.

The EERC had on hand approximately 25 tons of fresh uncrushed 2 x 0 Black Thunder coal from the Black Thunder mine acquired for use with the U.S. Department of Energy (DOE) joint venture project, "Pilot Plant Assessment of Blend Properties and Their Impact on Critical Utility Power Plant Components." Approximately 1000 pounds of this material was obtained for preparing the pulverized samples. This sample of 2 x 0 coal was first crushed to $-\frac{1}{4}$ in., then split into five subsamples using a rotating riffler. Each subsample was then separately pulverized to a utility grind of 68% -200 mesh. Prior to the subsamples being pulverized, a portion was first pulverized and a sieve analysis performed to verify that the proper size range was being obtained. The pulverized coal was collected in 55-gal drums double-lined with plastic, purged with nitrogen, and sealed. One of the drums was further subdivided by alternate scooping to obtain smaller samples (5-gal and 1-gal containers). The smaller samples were also placed in double-bagged containers, purged with nitrogen, and sealed.

Samples of the pulverized Black Thunder coal were sent to the University of Arizona, PSIT, Massachusetts Institute of Technology, the University of Kentucky, and Sandia National Laboratories. The EERC retained a sample for analysis and drop-tube furnace testing, along with the remaining pulverized coal as reserve sample and for future use. The EERC sample was submitted for proximate/ultimate, x-ray fluorescence (XRF), chemical fractionation, CCSEM, and included/excluded mineral analyses. The results of these analyses are given in Tables 3.1-1-3.1-5, as well as being distributed to the recipients of the coal samples.

Inorganic Transformation Studies.

Combustion tests have been performed in the drop tube furnace systems under standard and fuel-rich conditions in the drop-tube furnace system on Wyodak, Beulah, Upper Freeport, and Black Thunder coals. The Black Thunder coal was selected for ash transformation studies to be performed in collaboration with PSIT. The effects of low- NO_x conditions on ash transformations have been extrapolated from the fuel-rich combustion tests.

Experimental

Testing was performed in the atmospheric drop-tube furnace (ADTF) and optical drop-tube furnace (ODTF) systems. The two are basically similar, the ADTF being configured to determine combustion rates by gas analysis with collection of fly ash on bulk filters and the ODTF configured for growing deposits and in situ deposit strength measurements.

Both are laboratory-scale, entrained-flow, vertical drop-tube furnaces with the ability 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 ODTF is equipped with an optical section in which a deposition probe can be inserted. This optical section allows visual monitoring of

TABLE 3.1-1

Proximate/Ultimate Analysis Results for Black Thunder Coal

Parameter	As-Determined, wt%	As-Received, wt%
Proximate Analysis		
Moisture	8.71	24.30
Volatile Matter	43.29	35.88
Fixed Carbon	42.58	35.32
Ash	5.42	4.49
Ultimate Analysis		
Hydrogen	6.20	7.04 ¹
Carbon	63.75	52.84
Nitrogen	0.84	0.70
Sulfur	0.47	0.39
Oxygen	23.32	34.54 ²
Ash	5.42	4.49
Btu/lb	11604	9619

¹Not including hydrogen from moisture: 4.34%.²Not including oxygen from moisture: 12.91%.

TABLE 3.1-2

Bulk Inorganic Oxide Composition of Black Thunder Coal
As Determined Using X-Ray Fluorescence

Oxide	Ash Basis, wt%	SO ₃ -Free Ash Basis, wt%
SiO ₂	32.57	38.18
Al ₂ O ₃	16.81	19.71
Fe ₂ O ₃	5.69	6.67
TiO ₂	1.11	1.31
P ₂ O ₅	1.17	1.37
CaO	22.09	25.89
MgO	4.79	5.61
Na ₂ O	0.93	1.09
K ₂ O	0.15	0.17
SO ₃	14.69	---
Totals	100.00	100.00

TABLE 3.1-3

Chemical Fractionation Results for Black Thunder Coal
Normalized to Zero Silicon Loss

Element	Initial Conc., ppm	Weight Percent Removed			Weight Percent Remaining
		By H ₂ O	By NH ₄ OAc	By HCl	
Si	7751	0	0	0	100
Al	4529	0	0	20	80
Fe	2024	8	0	70	22
Ti	340	0	0	19	81
P	261	3	0	87	10
Ca	8033	1	58	39	2
Mg	1471	0	72	22	5
Na	350	22	64	10	4
K	62	15	0	0	85

TABLE 3.1-4

Mineralogy of Black Thunder Coal
As Determined Using Computer-Controlled Scanning Electron Microscopy

Mineral	Weight Percent by Size Category in Microns						Totals
	1.0 to 2.2	2.2 to 4.6	4.6 to 10.0	10.0 to 22.0	22.0 to 46.0	46.0 to 100.0	
Quartz	4.3	3.7	6.8	3.5	5.0	0.8	24.1
Iron oxide	0.4	0.6	1.4	0.9	1.3	0.0	4.6
Rutile	0.2	0.0	0.0	0.8	0.0	0.0	1.0
Alumina	0.0	0.0	0.2	0.0	0.0	0.0	0.3
Calcite	0.0	0.1	0.1	0.0	0.2	0.4	0.9
Dolomite	0.0	0.0	0.0	0.0	0.0	0.6	0.7
Kaolinite	3.9	8.4	6.2	4.8	3.8	1.9	29.1
Montmorillonite	0.4	2.0	0.7	2.1	1.1	0.8	7.1
K-Al Silicate	0.2	0.4	0.1	0.0	0.0	0.0	0.7
Fe-Al Silicate	0.0	0.3	0.1	0.0	0.0	0.0	0.4
Ca-Al Silicate	0.1	0.4	0.1	0.0	0.1	0.0	0.8
Aluminosilicate	0.2	0.9	0.5	2.5	0.1	0.5	4.6
Mixed Al Silica	0.1	0.1	0.3	0.0	0.0	0.0	0.5
Pyrite	0.5	0.0	0.1	2.2	0.6	1.4	4.7
Pyrrhotite	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Oxidized Pyrrhotite	0.1	0.0	0.0	0.0	0.2	0.0	0.2
Gypsum	0.0	0.2	0.0	0.0	0.0	0.0	0.2
Barite	0.1	0.2	0.4	0.0	0.0	0.0	0.6
Ca Al-P	1.6	3.1	4.0	0.9	0.2	0.0	9.8
Gypsum-Barite	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Si-rich	0.3	0.7	0.5	0.0	0.2	0.4	2.1
Ca-rich	0.0	0.0	0.0	0.0	0.1	0.0	0.1
Ca-Si-rich	0.0	0.1	0.0	0.0	0.0	0.0	0.1
Unknown	3.0	1.0	1.2	0.5	0.8	0.5	7.0
Totals	15.9	22.3	22.7	18.3	13.6	7.3	100.0

TABLE 3.1-5

Coal-Mineral Associations for Black Thunder Coal
As Determined Using Scanning Electron Microscopy

Mineral	Excluded, wt. %
Quartz	42.6
Iron oxide	54.8
Rutile	17.2
Alumina	15.8
Calcite	90.2
Dolomite	100.0
Kaolinite	42.8
Montmorillonite	63.3
K-Al Silicate	27.1
Fe-Al Silicate	0.0
Ca-Al Silicate	22.9
Aluminosilicate	53.2
Mixed Al Silica	51.9
Pyrite	77.9
Pyrrhotite	46.3
Oxidized pyrrhotite	15.3
Gypsum	84.7
Barite	40.4
Ca Al-P	19.3
Gypsum-Barite	46.4
Si-rich	4.7
Ca-rich	100.0
Ca-Si-rich	100.0
Unknown	29.1

deposit formation and in situ strength adhesion measurements of the deposit on the probe, as well as temperature measurements by optical pyrometry. Collection of entrained ash can also be performed in conjunction with deposition tests.

The furnace systems are designed for gas-flow rates of up to 5 standard liters per minute. Oxygen and nitrogen mass-flow controllers vary the oxygen concentration of the primary and secondary gas from 0% to 21%. Flowmeters split the gas mixture from the flow controllers between primary and secondary air. Approximately 1 L/min of the gas mixture is used for primary air, and the remaining is introduced into the furnace as preheated secondary air. The unheated primary air (used as the sample carrier gas) entrains the coal from the sample feeder and carries it through the injector into the furnace. The secondary air is preheated before it enters the furnace through the top of the reactor tube.

Both furnace assemblies consist of a 2½-in. ID alumina reaction tube heated externally by a series of tube furnaces. These furnaces possess a total of five

independently controlled, electrically heated zones. This provides maximum flexibility and precise control over combustion conditions. A preheat furnace heats the secondary air before it enters the reaction tube. A split-shell, two-zone furnace provides the heat for obtaining the desired reaction zone temperature. In the ODTF, a bottom furnace maintains the temperature of the collection zone located in the optical access section. Coal and primary air are introduced into the furnace system by a water-cooled injector. This injects ambient-temperature primary air and coal into the furnace at the center of the tube. Normal coal feed rates are 0.05–0.10 g/min. Secondary air is typically heated to 1000°C and introduced into the furnace through the top of the alumina tube and travels down through the tube around the injector. The material to be combusted is introduced into the furnace with the primary air through the injector and combines with the preheated secondary air. The coal and gas travel down the furnace in a laminar-flow regime.

For deposit production in the ODTF, the stream passes through an accelerator just above an optical access section where the deposition probe is located. The ash not adhering to the probe and the combustion gases flows into a water-cooled particulate collection probe located below the optical access section where it is quenched with nitrogen. The fly ash-quenching probe is attached to the bottom of the drop-tube furnace to cool the fly ash before collection. Bulk ash is collected on a filter after quenching.

The ODTF deposition probe is designed to simulate a boiler tube typical of those found in full-scale utility boilers. The probe is designed to maintain a sacrificial sample coupon attached to the probe at a specific temperature. This is accomplished by aspirating water with nitrogen in an inner shell that houses the coupon. Provisions have been made for achieving and controlling the coupon temperature over a broad temperature range by adjusting the nitrogen–water mixture in the deposition probe. The deposits are grown on machined stainless steel sacrificial coupons fitted into dovetailed slots on the top surface of the cylindrical deposition probe. The upper coupon surface is curved, matching the radius of the deposition probe. A hole is drilled in the end of the coupon aligned with a hole in the probe to accept a 0.020-in. type K thermocouple, which provides the temperature measurement. The probe is welded to the outer shell, and the inner shell consists of a series of annular tubes that provide the aspirated water to cool the probe end and also help keep the outer shell cool. The nitrogen and mist water flow back along the probe in the space between the inner and outer probe shells and exit to a drain line. The outer shell is insulated with a high-temperature insulation to minimize temperature loss in the optical zone and to help keep the shell from oxidizing. It also provides a sheath that covers the thermocouple leading to the coupon. A ceramic accelerator is used to accelerate the gas flow to approximately 15 m/s before it impinges on the deposit probe. The constrictor is made of a 1½-in.-thick disk of alumina insulation board (Zircar AL-30) 2–5/16-in. in diameter. A 0.25-in. hole is drilled in the center and beveled out from inside to approximately 45 degrees to form the nozzle. The deposit probe is located 1.0 in. below the constrictor.

The temperature of the coupon mounted on the probe is maintained at a selected temperature of 540°C to simulate a boiler heat-transfer surface in the fouling regime. Coupon temperature is monitored by a type K thermocouple in contact with the middle of the coupon, which provides feedback to regulate the probe-cooling air flow. Samples are tested in the ODTF to determine sticking coefficients, deposit strengths, and deposit compositions. The combustion conditions have been designed to mimic full-scale boiler

fouling and slagging conditions. Particle residence times and gas cooling rates can be varied to simulate specific slagging and fouling regions of interaction within the boiler.

Production of bulk fly ash samples from Black Thunder, Illinois No. 6, and Wyodak coals was performed in the ADTF under both oxidizing and two fuel-rich conditions at 0% and -50% excess air. The fly ashes collected were analyzed by thermogravimetric analysis (TGA), morphological examination using the scanning electron microscope (SEM), and by computer-controlled scanning electron microscopy (CCSEM) to determine particle-by-particle composition and mineral phases. Table 3.1-6 gives the experimental conditions for these tests. As is seen, the tests at 0% had some CO formed, but the bulk of the coal present had been converted to CO₂. At -50% excess air, the CO formed is equal to or exceeds the CO₂, indicating extremely reducing conditions. Also, the TGA analyses of Table 3.1-7 show that significant amounts of unburned carbon remained in the fly ash collected.

Mineral phases as determined by CCSEM analysis for the bulk fly ashes are given in Table 3.1-8. Because of the large percentage of "unknown" material (16.6% to 45.4%), specific trends of mineral transformations should be treated with caution. For the Black Thunder ash, the effect of fuel-rich conditions appears to be an increase in quartz, calcite, dolomite, and calcium-rich phases, along with a decrease in calcium-aluminosilicate phases. This may be the effect of the lower particle temperature and oxygen-lean atmosphere reducing the interaction and assimilation of pure quartz and organically bound calcium into mixed calcium-aluminosilicate phases. The large (45%) unknown category for the Black Thunder under full air conditions is indeed dominated by particles which are comprised predominantly of calcium, silicon, and aluminum. For the Illinois No. 6 ash, the fuel-rich conditions give a decrease in iron oxide, iron-aluminosilicates, mixed aluminosilicates, and iron silicate. There is a corresponding increase in pyrite and pyrrhotite (iron sulfides) and carbonate, which was absent under the full air conditions. The fuel-rich conditions appear to prevent the oxidation of pyrite and pyrrhotite to iron oxide, along with less assimilation of iron into mixed phases caused by the lower temperatures.

An alternative method of examining mineral matter transformations is given in Figures 3.1-1-3.1-8. Here, the cumulative percentage of the total particles by volume is plotted versus the elemental concentration for specific elements. This allows visualization of the general behavior of the element without using specific mineral categories, thus avoiding the problem of the "unknown" category.

For the Illinois No.6, calcium shows little change between oxidizing and fuel-rich conditions. Approximately 85% of the particle volume contains less than 15% calcium, and 15% of the volume contains greater than 80% calcium, with very few intermediate particles. By contrast, the Black Thunder shows 60% of the particle volume with calcium concentrations between 40% and 70% under oxidizing conditions. At 0% excess air, 60% of the particle volumes have little or no calcium, with the remainder having an evenly distributed increasing calcium concentration. At -50% excess air, the calcium concentration is separated with 60% of the particle volumes having little or none, and 25% having very high calcium concentrations of 60% or greater. The interpretation is that under oxidizing conditions (full air) in the Black Thunder ash there is extensive interaction of calcium with the aluminosilicates to form calcium-aluminosilicates between 60% and 80% calcium. At more fuel-rich conditions of 0% excess air, some interaction

TABLE 3.1-6

Experimental Conditions for the Inorganic Transformations Tests

Test ID	Fuel	Residence Time, s	Furnace Temperature, °C	Feed Rate, g/m	Primary Gas Flow, L/m	Secondary Gas Flow, L/m	O ₂ , %	Excess Air, %	CO/CO ₂ Ratio	Gas Carbon Conversion, %	TGA Combustion Conversion, %
268	Blk. Th.	~4	1500/1200	0.127	0.8	3.2	16.21	402	0.00	104.29	100.00
269	Blk. Th.	~4	1500/1200	0.132	0.8	3.2	0.09	-3	0.04	102.07	100.00
270	Blk. Th.	~4	1500/1200	0.127	0.8	3.2	-0.24	-50	3.02	92.69	98.17
271	Wyodak	~4	1500/1200	0.085	0.8	3.2	17.55	650	0.00	110.27	100.00
272	Ill. No. 6	~4	1500/1200	0.112	0.8	3.2	16.05	379	0.00	99.92	99.91
273	Ill. No. 6	~4	1500/1200	0.109	0.8	3.2	0.39	-2	0.02	96.91	94.73
274	Ill. No. 6	~4	1500/1200	0.109	0.8	3.2	-0.15	-51	1.44	73.63	80.18

TABLE 3.1-7

Thermogravimetric Analyses of Bulk Filter Fly Ash, wt %

	Black Thunder, full air	Black Thunder, 0% EA ¹	Black Thunder, -50% EA	Illinois No. 6, full air	Illinois No. 6, 0% EA	Illinois No. 6, -50% EA	Wyodak, full air
Moisture ²	0.15	0.45	0.64	0.18	0.15	0.25	0.01
Volatile Matter	0.00	0.00	0.95	0.33	0.98	1.38	0.00
Fixed Carbon	0.00	0.00	21.40	0.16	20.99	49.97	0.00
Ash	100.00	99.33	77.02	99.34	77.37	48.41	100.00

¹EA = Excess air.²Weight loss at 100°C in nitrogen.

TABLE 3.1-8

Mineralogy of the Bulk Filter Fly Ashes as Determined Using Computer-Controlled Scanning Electron Microscopy

	Black Thunder, full air	Black Thunder, 0% EA ¹	Black Thunder, -50% EA	Illinois No.6, full air	Illinois No.6, 0% EA	Illinois No.6, -50% EA	Wyodak, full air
Quartz	9.8	16.8	17.0	19.4	18.2	18.8	13.0
Iron oxide	0.7	2.5	0.8	10.7	6.2	0.8	0.7
Periclase	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.1	0.1	0.1	0.1	0.0	0.4	0.0
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Calcite	1.4	1.4	2.9	3.2	3.1	5.3	0.0
Dolomite	0.3	2.4	4.3	0.0	0.0	0.0	0.0
Ankerite	0.0	0.0	0.1	0.0	0.0	0.0	0.0
Kaolinite	4.5	11.5	7.0	4.4	7.1	4.8	1.9
Montmorillonite	1.1	2.8	0.7	6.6	7.6	4.9	2.5
K-Al Silicate	0.7	1.1	0.9	9.2	11.2	7.9	1.7
Fe-Al Silicate	0.2	0.1	0.1	7.9	6.0	3.0	0.3
Ca-Al Silicate	6.9	9.1	4.5	2.1	1.0	0.2	38.1
Na-Al Silicate	0.0	0.0	0.6	0.0	0.0	0.0	0.0
Aluminosilicate	0.7	2.6	0.8	3.1	3.0	0.8	1.5
Mixed Al Silica	0.7	0.4	1.2	4.4	2.8	6.8	2.7
Fe Silicate	0.0	0.0	0.0	1.9	1.0	0.3	0.1
Ca Silicate	4.7	6.0	5.7	0.1	0.4	0.5	1.2
Ca Aluminate	11.7	13.7	12.4	0.0	0.0	0.0	1.3
Pyrite	0.0	0.0	0.0	0.0	2.1	2.1	0.0
Pyrrhotite	0.0	0.1	0.0	0.0	3.1	7.6	0.0
Oxidized Pyrrhotite	0.0	0.0	0.4	0.1	0.8	2.0	9.0
Gypsum	0.0	0.0	0.0	0.4	0.0	0.3	0.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Apatite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca Al-P	0.0	0.3	0.5	0.0	0.0	0.0	0.1
KCl	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Al Silicate	4.8	0.0	0.7	0.0	0.0	0.0	0.8
Si-Rich	0.9	3.6	2.8	9.2	8.8	8.7	5.4
Ca-Rich	4.2	7.4	9.2	0.2	0.1	0.3	0.4
Ca-Si-Rich	1.3	1.2	1.0	0.2	0.2	0.1	0.1
Unknown	45.4	16.8	26.2	16.8	17.1	24.3	28.1

¹EA = Excess air.

still takes place, but to a lesser extent. Finally at -50% excess air, conditions are unfavorable for calcium-aluminosilicate interaction and favorable for formation of calcium oxide and carbonates; hence the division into particles with very low and very high calcium levels.

Iron in the Black Thunder coal is a relatively minor component, and little change is seen between full air and fuel-rich conditions. For the Illinois No.6 under full air, the iron concentration in the particle volumes is either quite low or quite high—less than 20% or greater than 80%. This is indicative of some interaction of iron with other species at low concentrations, along with the formation of iron oxide particles under the highly oxidizing conditions. Under fuel-rich conditions, the percentage of iron oxide decreases, with a concurrent increase in particles with intermediate (40%–80%) iron concentration, corresponding to pyrite and pyrrhotite.

For the Black Thunder ash under full air, the particles contain a broad range of silica concentrations, with only approximately 10% having no silica and another 10% as quartz. As conditions are made more fuel-rich, the degree of interaction decreases, with particles showing silicon concentration of either 0% or 40%–60% corresponding to aluminosilicates, and greater than 80% corresponding to quartz. A similar, but less pronounced trend is seen for the Illinois No.6 ash.

Aluminum concentrations remain nearly the same for both ashes under full air and fuel-rich conditions. Slight differences are presumably caused by the degree of interaction of other species with the aluminosilicates present.

Refining ATRAN Model

A model has been developed at the EERC for use as a research tool in predicting fly ash particle size and composition from CCSEM analyses of coal. The model, termed ATRAN as an acronym for ash transformation, is phenomenological, requiring detailed coal input data and empirically derived knowledge of inorganic transformation phenomena occurring during combustion. ATRAN, a stochastic model, simply combines initial coal inorganics in a random manner in order to predict the resultant fly ash particle size and composition. The model does not operate in a completely random manner, in that associations among coal minerals (i.e., locked versus liberated) influence the predictions. The ATRAN model is designed to emulate pulverized coal combustion and hence, use data derived from coals ground to 70%–80% -200 mesh. CCSEM data are used as the 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.

The ATRAN code for predicting the fly ash size and composition distributions from combustion facilities has undergone significant advancements in the last year. The FORTRAN version of the code was updated with a user-friendly graphical interface allowing easier use by researchers. The interface provides for convenient input of data and viewing of the results. In addition, a preliminary manual has been written detailing

Figure 3.1-1. Cumulative distribution of calcium in Black Thunder ash.

Figure 3.1-2. Cumulative distribution of calcium in Illinois No. 6 ash.

Figure 3.1-3. Cumulative distribution of iron in Black Thunder ash.

Figure 3.1-4. Cumulative distribution of iron in Illinois No. 6 ash.

Figure 3.1-5. Cumulative distribution of silicon in Black Thunder ash.

Figure 3.1-6. Cumulative distribution of silicon in Illinois No. 6 ash.

Figure 3.1-7. Cumulative distribution of aluminum in Black Thunder ash.

Figure 3.1-8. Cumulative distribution of aluminum in Illinois No. 6 ash.

the operating instructions. In addition to the FORTRAN version, ATRAN was ported and recoded into the more efficient and powerful C language. The new C version, which does not yet contain a user-friendly interface, is designed for incorporation into other models in a modular manner. Conversion to C resulted in a significant increase in performance; the C version will run in approximately 25% of the time required by the FORTRAN version. In addition to optimization, the C version was also enhanced to allow for up to five blends of coal and three-magnification CCSEM data files. Previous versions of ATRAN accepted only a blend of two coals, which was limiting in some applications. The allowance for three-magnification CCSEM data was necessary to utilize the newest forms of data. The CCSEM technique was updated from two magnifications to three magnifications to allow for better sample statistics and thus better data. It is expected that the C version will shortly be equipped with a user-friendly graphical interface similar to that of the FORTRAN version.

Development of Advanced Analytical Methods

Round-Robin Study of the Computer-Controlled Scanning Electron Microscopy Method of Coal Mineral Analysis

A round-robin study designed to evaluate the CCSEM method of quantitative coal mineral analysis was initiated in April, 1992. Seven laboratories, listed in Table 3.1-9, are participating in the project. Each laboratory is expected to perform a total of five analyses on three prepared coal samples—polished epoxy mounts of the Illinois No. 6 and Pittsburgh No. 8 coals from the Argonne Premium Coal Sample Program (1, 2) and Prince coal from the European Centre for Coal Specimens. The data obtained will be used to assess the performance characteristics (repeatability and reproducibility) of CCSEM.

Analysis progress for the round robin is summarized in Table 3.1-10; six laboratories have analyzed the Pittsburgh No. 8 coal and three laboratories have analyzed the Illinois No. 6 and Prince coals. A statistical analysis of the results will be performed when all the results have been obtained.

Assessment of Fine-Particle Analysis Technique

Electron microscope techniques are commonly applied to coal mineral and ash particles with minimum diameters of 1 μm . However, individual particle analysis is also important for submicron ash particles that form during combustion from both organically associated elements and from minerals in coal. Organically associated elements in low-rank coals, including Na, Mg, and Ca and, to a lesser extent, K, Fe, and Al, commonly vaporize during combustion. Na, Mg, and K 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 SO_2 to form submicron sulfate particles by the time they reach the outlet of the boiler. Mineral particles in coal undergo much less vaporization and condensation during combustion. The extent 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, SiO_2 can be reduced to 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 Na species. Submicron particles can also be produced through size reduction of larger mineral particles when decomposition or fragmentation occurs during heating.

TABLE 3.1-9

CCSEM Round-Robin Participants

Laboratory	Manager
Ames Laboratory Iowa State University, USA	Dr. Warren Straszheim
CSIRO Division of Mineral & Process Engineering, Australia	Dr. Paul Gottlieb
Netherlands Energy Research Foundation (ECN), Netherlands	Dr. John Vleeskens
Energy & Environmental Research Center (EERC) University of North Dakota, USA	Mr. Kevin Galbreath
University of Kentucky, USA	Dr. Gerry Huffman
R.J. Lee Group, Incorporated, USA	Dr. Gary Casuccio
Sandia National Laboratories, USA	Dr. Nancy Yang

TABLE 3.1-10

Laboratory	Analysis Progress		
	Pittsburgh No. 8	Illinois No. 6	Prince
AMES	IP ¹		
CSIRO	AC ²	AC	AC
ECN	AC		
EERC	AC	AC	AC
U. Kentucky	AC	IP	IP
R.J. Lee	AC	AC	AC
Sandia	AC		

¹IP = Analysis in progress.²AC = Analysis completed.

When rapidly heated, pyrite fractures and, upon partial oxidation, forms FeS fragments before melting at 1075°C (3). Calcite (CaCO_3), siderite (FeCO_3), and ankerite ($\text{Ca,Fe}(\text{CO}_3)_2$) also fragment upon decomposition to form submicron particles (3). Once formed, submicron particles are difficult to remove from the flue gas stream. When emitted, these fine particles contribute far more to plume opacity per unit mass than do larger particles (4). 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 (5, 6). Understanding the composition and formation of submicron particles is thus important in mitigating particulate emissions.

Submicron particles are difficult to analyze with automated techniques because their small size places them near the imaging and analytical detection limits of the conventional scanning electron microscope. Using a new sample preparation method involving freeze drying, individual ash particles with diameters as small as 0.1 μm can be analyzed automatically in the Tracor-Northern automated digital electron microscope (ADEM). The new technique is termed scanning electron microscopy with image analysis (SEM-IA) and is generally similar to CCSEM. Details of the technique and test results have previously been described (7, 8).

SEM-IA results clearly indicated a size-related shift in composition, from mineral-rich particles in the supermicron fractions to sulfate-, phosphate-, and chloride-rich particles in the submicron fractions of both Eagle Butte and Eagle Butte/Kentucky No. 9 blend ashes. 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. The unique compositions of particles in the submicron fraction suggest that individual particle analysis of these smallest particles is essential to achieving an overall understanding of the transformations occurring during combustion. The SEM-IA technique and detailed results were the basis of a paper presented at the 1993 American Chemical Society national meeting (8).

Development of Particle-by-Particle Scanning Electron Microscopy Method of Coal Mineral Characterization

Introduction

The physical and chemical properties of minerals that control their behavior during coal combustion 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 subsequent 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 (9, 10). 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 the SEM for quantifying the association of mineral grains with the organic coal matrix.

The particle-by-particle scanning electron microscopy (PBPSEM) method was developed to size, identify, and quantify coal minerals and their degree of association with the organic matrix. The method utilizes an automated digital electron microscope to measure various morphological and compositional parameters for individual mineral grains in coal. A sample of Black Thunder coal was analyzed by PBPSEM and preliminary analysis results are presented.

Description of the PBPSEM Method

Sample Preparation and Instrumentation

The Black Thunder coal was pulverized to a standard combustion grind (i.e., approximately 80 % of the particles -200 mesh), mounted in carnauba wax (11), cross sectioned, and polished using standard petrographic procedures (12). The sample was then sputter-coated with carbon to minimize electron-beam charging artifacts. The analysis was conducted on a Tracer-Noran ADEM.

Digital Image Acquisition, Processing, and Analysis

The ADEM was operated at a magnification of 500 to provide the spatial resolution necessary to analyze particles ranging widely in size. Digital backscattered electron (BSE) images were acquired at 17 different locations on the sample at a spatial resolution of 512 pixels in both the line-scan (x-) and frame-scan (y-) directions. Frame averaging was employed to enhance image quality. Coal and mineral particles were delineated based on the atomic number contrast inherent in BSE imaging (13). Standard image analysis techniques (14) were used to determine the following morphological parameters for each phase of a given particle: minimum, maximum, and average cross-sectional diameter; area; and external perimeter. Two correlation parameters were also determined for each mineral phase: an indication of whether the mineral grain was included or excluded relative to the coal matrix and the amount of mineral perimeter in contact with the coal or mounting medium. In addition to these morphological and phase correlation data, compositional information was obtained by acquiring an energy-dispersive x-ray (EDX) spectrum from the center of each mineral grain. Spectral regions of interest were 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). The acquired data were transferred to a personal computer and stored to disk for subsequent reduction, report generation, and archiving.

Data Reduction and Reporting

A modified PARTCHAR data reduction program (9, 10) classified the mineral compositional analyses based on elemental relative intensities, relative intensity ratios, and stoichiometric criteria into mineral categories. The program produces a report that summarizes the results in a series of tables containing information on the number, area, and proportions of mineral phases in their respective size intervals and according to their association with the coal matrix (i.e., percent excluded). Mineral weight percentages were calculated assuming that particle area is proportional to particle volume (15) and mineral densities are constants.

Results

A total of 1004 particles, 190 mineral and 814 coal particles, were analyzed. Analysis results are presented in Tables 3.1-11 and 3.1-12. These results, however, are statistically insignificant because of the limited number of mineral particles analyzed. The image analyzer employed is unable to efficiently collect the large amount of data required to adequately characterize coal mineralogy. Approximately ten hours of instrument time were required to analyze the 1004 coal and mineral particles.

The PBPSEM analysis results are compared to CCSEM results in Figures 3.1-9, 3.1-10, and 3.1-11. The quantitative mineralogy results compare favorably, whereas the particle size and image analysis results do not. Some of the variation is attributable to large differences in the sample populations, 190 mineral grains for PBPSEM versus 969 grains for CCSEM. Additional PBPSEM mineral analyses must be obtained before a valid statistical comparison can be performed.

Conclusions

The PBPSEM analysis method has been developed to provide detailed morphological and compositional information on the minerals in coal. The method in its current state of development is a research tool and cannot be used routinely for characterizing coal mineralogy. However, the results of the PBPSEM analysis results compare fairly well to the standard CCSEM analysis, considering the disparity in particle sample size.

Ash Transport and Deposit Initiation and Growth

The specific goals for the first year were to 1) conduct a literature search on the areas of ash transport, deposit initiation, and ash deposition; 2) perform modifications to the ODTF, including a fourth furnace, convective pass simulator, gas analyzers, and improved computer control and image analysis capabilities; 3) perform studies of deposit initiation; 4) develop transport algorithms to determine sticking fractions of entrained particulate; and 5) determine deposit growth rates.

Literature Search of Ash Transport, Deposit Initiation, and Ash Deposition

As part of the program to develop an understanding of ash transport and deposition, as well as to assist in the development of the transport algorithms, a literature search was conducted covering the topics of ash transport, deposit initiation, and ash deposition. Data from the literature supplement the ongoing experimental deposition program, and literature transport and deposition models will be examined for approaches and features of interest to the ash transport and deposition algorithms under development. The literature survey has been completed covering the most significant recent literature, a summary of which was given in the June 1993 semiannual report.

Modifications to the ODTF

The ODTF is a laboratory-scale, entrained-flow, vertical downfired tube furnace with the ability 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 is equipped with an

TABLE 3.1-11

Quantitative Mineralogy of Black Thunder Coal, wt% on a mineral matter basis

	Particle Diameter, μm						Total
	1.0	2.2	4.6	10	22	46	
	to 2.2	to 4.6	to 10	to 22	to 46	to 100	
Quartz	0.2	3.3	9.6	12.3	12.6	ND	38.0
Calcite	ND ¹	0.1	0.7	0.8	ND	ND	1.6
Kaolinite	0.3	3.6	4.2	9.6	19.8	ND	37.5
Smectite	ND	0.4	0.9	2.5	4.6	ND	8.4
Illite	ND	0.2	ND	ND	ND	ND	0.2
Pyrite	ND	ND	ND	ND	6.9	ND	6.9
Apatite	ND	ND	ND	2.8	ND	ND	2.8
Others	0.1	1.6	2.9	ND	ND	ND	4.6
Total	0.6	9.2	18.3	28.0	43.9	0	100

¹ND = not detected.

TABLE 3.1-12

Coal Mineral Association Relationships for the Black Thunder Coal, % excluded

	Particle Diameter, μm					
	1.0	2.2	4.6	10	22	1.0
	to 2.2	to 4.6	to 10	to 22	to 46	to 100
Quartz	0	11.2	46.6	74.5	100	70.0
Calcite	NA ¹	100	100	100	NA	100
Kaolinite	25.0	32.2	40.5	90.0	72.0	68.9
Smectite	NA	0	33.3	100	100	88.6
Illite	NA	100	NA	NA	NA	100
Pyrite	NA	NA	NA	NA	100	100
Apatite	NA	NA	NA	100	NA	100
Others	0	40.3	54.0	NA	NA	47.6

¹NA = not applicable.

Figure 3.1-9. Comparison of PBPSEM and CCSEM Black Thunder Coal mineral analysis results.

Figure 3.1-10. Comparison of PBPSEM and CCSEM Black Thunder Coal image analysis results.

Figure 3.1-11. Comparison of PBPSEM and CCSEM Black Thunder coal mineral size analysis results.

optical section in which a deposition probe can be inserted. This optical section allows visual monitoring of deposit formation and in situ strength adhesion measurements of the deposit on the probe as well as deposit temperature measurements by optical pyrometry. Collection of entrained ash and process gas analyses can also be performed in conjunction with deposition tests.

A fourth high-temperature furnace has been installed on the ODTF. This allows longer particle residence times and higher particle velocities. At the same time, several other minor modifications and improvements were made. A prototype of the convective pass simulator (CPS) for the ODTF has been fabricated. The purpose of the CPS is to trap and remove the larger particulate material in the high-temperature region of the furnace, while allowing finer particulate material to continue on and impact the deposition probe. This will more closely simulate the conditions in the convective pass of a utility boiler. The CPS is a ceramic single-stage impactor that can be readily inserted and removed from the main furnace tube. Larger particles will be collected in a removable impactor cup, probably as a slag, while the smaller particles will follow the gas stream and impact the probe. Testing of the CPS will be done as part of currently ongoing projects investigating ash transformations and deposition. Improvements to the computer control of the ODTF have been made, including installation of data acquisition and control interfaces and software and an interface to allow the computer to monitor and control the coal feed rate.

Deposit Initiation Studies

Of particular interest in the process of coal ash deposition on heat-transfer surfaces is the manner by which an ash deposit first begins to form—the initial adhesion of ash particles to the metal heat-transfer surfaces. Ash deposition occurs by the mechanisms of inertial impaction, thermophoresis, and condensation. Of these, inertial impaction is the dominant mode of deposition and of primary interest. Fundamental studies by Austin and others first identified the factors contributing to the sticking of coal slags to steel surfaces (16–21). The factors included both particle substrate composition and temperature. Subsequent studies examining deposit initiation in a drop-tube furnace using actual coals were performed by Abbott and Austin (22) and Benson and Austin (23). Particles with significant concentrations of iron, iron and sulfur, iron and silicon, calcium and sulfur, calcium and phosphorus, barium, barium and sulfur, and strontium and sulfur were found to form strongly adhering initial deposits. Srinivasachar, Helble, and Boni (24), in experiments with synthetic ashes and a San Miguel coal under effectively slagging conditions, identified particle viscosity as the dominant factor in ash deposition. Further, they identified a critical viscosity above which little or no deposition occurred and noted that the critical viscosity for adhesion was inversely proportional to particle kinetic energy. It should be noted, however, that particle impaction efficiency is directly proportional to particle size and mass. Thus the process of deposition may be seen as a process between the competing requirements for particle impaction and particle adhesion.

The primary objectives of this research were to investigate the key factors in ash deposit initiation during pulverized coal combustion. Several conclusions were drawn from this work, including the following:

- Oxygen concentration appears to have only a minor effect on deposit initiation. Such effects may be partial reduction of iron species at low oxygen concentrations and increased agglomeration of mineral species caused by higher combustion temperatures at high oxygen concentrations.
- Seven general species make up the bulk of the initially adhering particle compositions. These are iron species, iron–calcium, iron–silica, iron–silica–alumina species, calcium–silica–alumina species, barium, and barium sulfate species.
- The initially adhering species are common to all coals, with particle abundance being governed by concentration in the original coals.
- The great majority of the initial ash particle masses and viscosities cluster in a grouping above a certain critical mass and below a certain critical viscosity regardless of individual composition. This indicates that the initial adhering particles are those with sufficient kinetic energy to impact the substrate and sufficiently low viscosity to adhere upon impaction.
- Propensity for the initial ash deposition can be roughly related to the fraction of particles in the bulk fly ash possessing these required mass and viscosity requirements. However, the effect of volatilized or organically bound inorganic material is not assessed by this relationship.

Details of the experimental methodology, results, and conclusions of the deposit initiation studies have been presented as a paper published in a special issue of *Energy and Fuels* (25).

Development of Transport and Deposition Algorithms

The ash formation and deposition algorithm development effort under the Fuels Utilization Properties (FUP) project is very limited because of program changes at the EERC. Therefore, in this report we will only be able to generally outline what we feel is an acceptable approach to developing ash deposition algorithms in the future. The algorithms described in this work to date are intended as research tools to better understand the ash deposition process and are a combination of written explanations of ash deposition mechanisms and mathematical expressions. Initially, the FUP program was to last five years and a model would have been devised, as a research tool, for understanding the fundamental mechanisms of pulverized coal ash deposition. The focus of the EERC Cooperative Agreement projects, however, has been shifted to short-term projects pertaining to advanced combustion systems. In general, ash deposition algorithms should consider the fluid dynamic conditions in the vicinity of the surface as well as the physical and chemical properties of the inorganic material. The inorganic transformations during the combustion process and during entrainment in the gas stream do not necessarily need to be considered; i.e., the physical and chemical properties of the entrained inorganic material before the deposition process occurs can be considered fixed. Similarly, the system operating parameters, such as gas and surface temperatures and gas flow, which control the initial fluid dynamics of the deposition process, can be defined rather than calculated. However, coding should be in a modular form to allow future integration into a larger, more comprehensive system.

Background

Models that incorporate rigorous ash transformation and deposition algorithms dealing with combustion and combustion systems are abundant in the literature. Their complexity ranges from the exhaustively comprehensive and ponderous 87-PCGC-2 and 90-PCGC-3 simulations developed by Brigham Young University to mechanistic models such as Ash Deposit Local Viscosity, Index of refraction, and Composition (ADLVIC) being developed by Baxter (26), and LEADER (27, 28) being developed by the EERC to the EERC PCQUEST (29), which is a set of slagging and fouling indices based on coal properties and experience. The goal of the FUP modeling effort is to develop a model that will act as a research tool to address deposition as comprehensively as possible, while remaining fast and easy to use.

The EERC has previously developed several models relating to ash transformations and combustion, including PHOEBE (30), PCQUEST, ATRAN1, LEADER (27, 28), and the FOULER portion of the EPRI Coal Quality Expert (CQE) model, scheduled for release in late 1994. The EERC also has coded the slagging algorithms for the CQE model in cooperation with Physical Sciences Incorporated and Black and Veatch. Experience gained during the development of the CQE FOULER project has been the most applicable to the FUP algorithm development. The FOULER algorithms are considerably simplified because of the execution time constraints placed on FOULER by the main CQE model. In particular, the time dependence of deposit properties such as strength and thermal

conductivity is handled with empirical equations defining trends rather than actual recursion and recalculation.

The EERC has a large database of information relating to ash and ash deposition from which to draw upon in formulating the ash deposition algorithms in the future. Information from bench- and pilot-scale tests is available, as well as the results from field tests performed by the EERC, such as those for Project Calcium.

Approach

The algorithm development is to be the basis of a future mechanistic model which should be versatile—able to be used with systems having several deposition geometries and covering a wide range of temperatures and surface materials. Ash deposition models should be as comprehensive and accurate as possible, accounting for several deposition mechanisms and employing "best values" from the literature as well as the results of bench-, pilot-, and full-scale combustion test data. A simplified algorithm could be developed based on inertial impaction of fly ash on a cylindrical boiler tube. The probability of impaction is done on a particle-by particle basis using the inertial impaction correlations developed by Wessel and Righi (31). At present, only centerline impaction need be considered, with an adjustable empirical constant used to account for off-centerline impaction. Particles with suitable kinetic energy for impaction then have a probability of sticking assigned, based on their kinetic energy and viscosity. The sticking criteria are derived from the work of Srinivasachar, Helble, and Boni (24). Empirical results from the deposit initiation studies could be included to define the critical kinetic energy and viscosity, which in turn define the minimum conditions whereby the particle adheres. Analysis of deposits grown under various conditions in the drop-tube furnace system could be used to provide a means of including the assimilation of nonsticky particles of high viscosity impacting very sticky low-viscosity surface particles. This would be a probability based on particle viscosity, kinetic energy, and ratio of low-viscosity to high viscosity particles in the deposit.

Deposit Strength Development and Thermal Properties

The specific goals for the first year were to 1) conduct a literature review of silicate and sulfate sintering behavior, 2) conduct sintering and deposit thermal conductivity experiments, 3) develop a first-order correlation between deposit physical and chemical properties and deposit growth rates, strength development, and removability, and 4) develop a first version of a deposit conductivity algorithm.

Literature Review of Silicate and Sulfate Sintering and Deposit Thermal Properties

Of prime importance and interest are the physical properties of fouling and slagging deposits that impact boiler performance. These properties include thermal conductivity, emissivity, reflectivity, and strength. All are a function of both deposit composition and the time-temperature history of the deposit.

In recent years, modeling efforts have increased, as well as experimental studies at the laboratory-, pilot-, and full-scale level to obtain fundamental data on the properties of ashes and slags. Such work provides a basis for additional experimentation and model

development, as deposit physical properties are a complex interactive result of ash size and chemistry. The following is a review of the current state and direction of experimentation and modeling of ash deposit physical properties.

Deposit Thermal Conductivity

Deposit thermal conductivity and strength are interrelated, as both are a consequence of the degree of sintering and melting of the deposit. Both depend on the physical state of the deposit, i.e., the degree of sintering and porosity, and only indirectly on chemical composition. The thermal conductivity of the ash particles themselves is almost independent of chemical composition. The primary role of ash chemistry arises from the ash viscosity and interactions that control the degree of sintering and melting in the deposit.

Thermal conductivity of laboratory ash as a function of temperature and particle size has been measured by Mulcahy, Boow, and Goard (32, 33) and Boow and Goard (34). Ash deposit thermal conductivities have been obtained by Wall et al. (35) and Benson et al. (36). The results show that the thermal conductivities of unsintered ashes are very low. A special case occurs with very fine material (< 1 micron) when the pore sizes become on the order of the mean free path of gas molecules, and the thermal conductivity may be less than that of air (37, 38). The deposit thermal conductivity is nearly linear with temperature until the onset of sintering occurs. Partial or complete sintering results in an abrupt increase in thermal conductivity. Further, the increase in thermal conductivity is not reversible on cooling, which results in a conductivity parallel to but higher than that of the original sample. The ultimate effect of increasing temperature is to produce a dense, effectively homogenous slag. The thermal conductivity of this material may be considered as an upper limit for nonmolten ash deposits.

Deposit Strength

Two types of deposit strength are of interest: the strength of adhesion of the deposit to the heat-exchange surface and the strength of the deposit itself, which for removal purposes is the shear strength. Adhesion of initially impacting ash particles to a metal substrate and the mechanisms of the formation of an initial ash deposit have been fairly well studied and understood. The strength of the deposit itself is related to the deposit composition, the current deposit temperature, and the deposit time-temperature history. The effect of deposit composition is based on the viscosity and interaction of the mineral phases present, impacting the degree of sintering that occurs. Currently, experimental data on deposit strengths at temperature are sparse, as well as information on the relationship between deposit composition and degree of sintering.

The factors influencing the adhesion of ash particles to steel surfaces were first identified by fundamental studies of Austin and others that examined the sticking of coal slags to steel surfaces (16-21). Subsequent studies examining deposit initiation in a drop-tube furnace using actual coals were made by Abbot and Austin (22) and Benson and Austin (23). Particles with significant amounts of iron, iron and sulfur, iron and silicon, calcium and sulfur, calcium and phosphorous, barium, barium and sulfur, and strontium and sulfur were found to adhere strongly. That ash viscosity is the dominant factor in ash deposition, with a critical point above which no ash deposition occurs was found by Srinivasachar, Helble and Boni (24). The critical viscosity was also found to be inversely

proportional to particle kinetic energy. Studies by McCollor, et al. (25) examining ash deposit initiation show that the propensity for initial ash deposition can be related to the fraction of particles in the bulk fly ash possessing the required viscosity and kinetic energy. Measurements of the adhesion strength of ash deposits in situ in a drop-tube furnace under fouling conditions have been performed by Zygarlicke et al. (39). Empirical correlations of adhesion strength with an independent index of fouling behavior were found. Pilot-scale in situ measurements of deposit bond strengths have been performed by Linder, et al examining the effect of mineral additives (40).

The strength of deposit material itself has been examined in detail by conventional tests, such as compressive strength tests (41). Unfortunately, these tests have been performed primarily at room temperature. Under such conditions, all mineral phases of the deposit are solids and the strength obtained represents an upper-limit case. In actuality, at elevated temperatures, a percentage of the deposit minerals will be of low viscosity, tending to decrease the deposit strength.

Deposit Optical Properties

The optical properties of deposits have a significant effect on heat transfer, particularly in the radiant section of a utility boiler. The increased utilization of western low-sulfur coals has underscored this, as the ash from these coals can prove to be more reflective, significantly reducing radiant heat transfer (42). Further, since the optical properties of interest—emittance, absorbance, and reflectivity—are surface properties, only a fairly thin deposit layer is needed to affect the radiant heat transfer. Both the chemical and physical properties of the deposit influence optical properties. Characterization of deposit optical properties have proceeded by both experimental laboratory and in situ measurements and the development of predictive models based on Mie scattering from small particles. An inescapable difficulty is that deposits are rough, heterogenous material not well suited to either experimental measurements or to modeling from fundamental optical principles.

The measurements of the total emittance of ashes by Boow and Goard (34) indicate that emittance decreases with increasing temperature until sintering and fusion occur, after which emittance increases. Emittance also was found to increase with particle size and iron and carbon content. Other measurements such as those of Mulcaly, Boow, and Goard (32) and of Goetz et al. (43) of slags indicate very high emittance values for completely sintered material. Further data are presented in the reviews by Wall, et al. (35, 44, 45).

Calculation of Mie absorption and scattering by small particles has been developed by Bohren and Huffman (46). Other calculation methods include a two-flux method developed by Bohren (47), and a discrete ordinate method by Chandrasekhar (48). Comparison of calculations using these methods with experimental data compiled by Wall et al. (45) indicates that the multiple scattering method (48) can give semiquantitative predictions.

Sintering and Deposit Thermal Conductivity Measurements

Eight coals were selected to test the effects of coal quality and deposition conditions on fouling deposit removability. The coals included a wide range of known full-scale fouling deposition behavior. The Beulah lignite from North Dakota and Anderson-Dietz subbituminous coal from Montana are high-alkali coals notorious for causing fouling problems. The Wyodak coal from Wyoming is a moderately fouling subbituminous coal. A 70% Wyodak and 30% bituminous Oklahoma Croweburg blend, termed "Wyodak 70/30 blend," also has intermediate or moderate fouling tendencies. Two bituminous Illinois coals, one termed "Illinois A," which consisted of a mixture of Illinois No. 2, No. 3, No. 5, and No. 5a coals and the other termed "Illinois B," which consisted of Illinois No. 6 coal only. The final coal used was a bituminous Western Kentucky No. 11. All four bituminous coals were known as fairly low-fouling coals from field experience. An initial set of deposits, termed "Group I," were grown while establishing test protocols and conditions. With test procedures established and standardized, a second series of deposits, termed "Group II," were grown for study.

The fouling deposit adhesion tests were conducted in the ODTF with the adhesive strength of the deposits measured in situ. The adhesion tests were undertaken on the test coals to systematically examine the effect of key variables on deposit adhesion strength. For ash deposits grown under fouling conditions from a Beulah coal, the in situ deposit adhesion strengths determined were found to be correlated with $1/\text{feed time}$, number of sootblowings, and (noneffective sootblowings)². By taking into account the coal high-temperature fouling index, a similar good correlation was found for several other coals. A similar, but lower, correlation was found for older Group I coals for which coupon temperature, $1/(\text{bake time} \cdot \text{noneffective sootblowings})$, the high-temperature fouling index, and (relative high-temperature fouling index)² were contributing factors. Room-temperature crushing strengths for the Group II deposits were found to be correlated with the high-temperature fouling index, the deposit growth time, and whether the deposit was sootblown or not. A moderately good correlation between in situ adhesion strength and room-temperature crushing strength was found.

The inverse dependence of deposit adhesion strength on coal feed time appears to reflect the degree of adhesiveness of a given deposit. A long feed time corresponds to the deposit being repeatedly removed by sootblowing until a sufficiently tenacious base has accumulated. Such a deposit would be expected to have a low adhesion strength. Conversely, a deposit that quickly adheres well enough not to be removed by sootblowing would have a higher adhesion strength. Coupled with the coal feed time is the total number of sootblowings, since longer feed times result from the deposit being repeatedly removed by sootblowing. Each sootblowing also appears to remove loosely adhering ash, allowing the gradual accumulation of ash more firmly anchored to the substrate. Once the deposit is no longer removed by sootblowing, additional sootblowings no longer contribute to strengthening the deposit adhesion and may actually weaken it because of thermal shock.

The development of deposit crushing strength proceeds somewhat differently from that of adhesion strength. The negative correlation of crushing strength with sootblowing suggests that sootblowing may thermally shock the deposit, weakening the crushing strength. The deposit growth time also has a negative correlation with deposit crushing strength. This may be explained by rapid deposit growth reflecting lower ash viscosities

and a higher degree of fusing, which, upon cooling, would result in a higher crushing strength.

Both deposit adhesion strength and crushing strength are correlated with the independently derived fouling index, based on the concentrations of inorganic constituents notable for causing fouling deposits. Coals with abundant alkali-alkaline-earth inorganics present typically show severe fouling behavior. For example, the Beulah lignite contains significant organically bound sodium that enters the vapor phase early in the combustion process and subsequently condenses on the cool deposit surface and reacts with aluminosilicate particles deposited by inertial impaction. These fine particles act to depress the melting points of the silicates present in the deposit, creating highly sintered and stronger deposits.

The results have shown that both deposit adhesion and crushing strength can be related to an index of coal fouling propensity in a utility boiler. However, several interrelated deposition test conditions also were found to contribute strongly to measured deposit adhesion and crushing strengths, even for a single coal type. Because of this interdependence, the analysis procedure does not select the same variables in every case. The important consideration, though, is that strength is related to deposit sootblowing and to bake time. Two general conclusions can be drawn. First, the interpretation and use of deposit strength determinations must be done with caution. Second, specific operating conditions in a full-scale boiler will have a significant impact on the properties and behavior of ash deposits for a specific coal. These results have been presented at the Engineering Foundation Conference in Solihull UK (39).

Effect of Fuel Rich Conditions on Deposit Properties

Deposits of Black Thunder and Illinois No.6 were grown under fouling conditions with both conventional "full air" and fuel-rich (0% excess air) to assess the effect of fuel rich conditions on deposit formation and strength. Table 3.1-13 gives the results of the deposit tests. In the table, the sticking coefficient is defined as the ratio of the weight of the ash deposit to that of ash fed. The growth factor is the ratio of the weight of the ash deposit to that of the total ash collected (the weight of deposit and weight of ash collected in the backup filter). Because of occasional losses of ash in the system, the growth factor is generally the most reliable. Both the sticking coefficient and growth factor are nearly constant with time, as the deposit formed approximates a cylinder with growth occurring on a constant cross-sectional area at the top. Deposit strengths were obtained as crushing strengths after the deposits were removed from the furnace and cooled.

There was no appreciable difference in sticking coefficient or growth factor between the oxidizing and fuel-rich conditions for either the Black Thunder or the Illinois No.6 deposits. This would suggest that the deposition is controlled by the "stickiness" of major phases present but not affected by fuel-rich conditions and that reduced species play a minor role in the deposition process under these conditions. The crushing strengths of the deposits covered a wide range because of the onset of sintering in some of the deposits. Despite this, the Black Thunder deposits appeared to be substantially weaker when formed under fuel-rich conditions and the Illinois No.6 deposits slightly stronger.

TABLE 3.1-13

Properties of Black Thunder and Illinois No.6 Deposits				
	Black Thunder		Illinois No.6	
	Full Air	0% EA*	Full Air	0% EA
Sticking Factor				
Average	0.43	0.39	0.34	0.27
Standard Deviation	0.04	0.02	0.03	0.02
Growth Factor				
Average	0.62	0.63	0.45	0.46
Standard Deviation	0.05	0.01	0.03	0.01
Crushing Strength				
Average	800	208	146	174
Standard Deviation	342	113	85	8

*EA = Excess air.

Deposit Sintering Strength Experiments

Experiments were undertaken in an attempt to find a preliminary relationship between the degree of deposit sintering and deposit strength development. In conjunction with another project, hopper ash from a utility power plant burning Eagle Butte coal was used for sintering tests. The ash was sieve-sized into fractions $<20\mu\text{m}$ and $>20\mu\text{m}$ and formed into pellets. The pellets containing the $<20\mu\text{m}$ ash were sintered under low-temperature conditions of 704°C and 982°C for 2, 6, and 10 hours in an atmosphere containing SO_2 in concentration similar to that of a combustion gas. The pellets containing the $>20\mu\text{m}$ ash were sintered under high-temperature conditions of 1093°C and 1204°C for 2, 6, and 12 hours in a similar atmosphere. The sintered pellets were then placed in a compression strength testing apparatus, heated to the temperature at which they were sintered, and compressive strength determinations made.

In principle, a material under compression will exhibit a characteristic strain-versus-stress behavior—a linearly increasing region with a slope proportional to the modulus of elasticity of the material. At some point, the proportional limit, the material will no longer show increased strain as increased stress is applied. Although the property of interest for ash deposits is shear strength, compressive strength can be related to shear strength (49). In practice, the stress-strain curves of the deposits under compression did not exhibit simple behavior; rather, complex plots indicated that several effects were involved. Further, the plots were quite "noisy," possibly because of the breaking of localized sintered regions within the deposit rather than the deposit uniformly exhibiting strain. Overall, the reproducibility was rather poor. It was concluded that compressive strength measurements would not provide a useful measurement of ash strength development caused by sintering without a detailed and systematic examination of the effects and variables involved.

Development of a Deposit Conductivity Algorithm

A first-order algorithm relating deposit thermal conductivity to temperature and the degree of deposit sintering has been developed with empirical numerical constants based on the data of Mulchay, Boow, and Goard (32). Effective thermal conductivity is estimated by a linear equation as a function of temperature over the range before the onset of sintering. The slope and intercept of these lines are determined by extrapolation between the unsintered and fully sintered cases for the Mulchay data. A second linear equation is used when the temperature reaches or exceeds the onset of sintering, where the effective thermal conductivity increases rapidly. The conductivity also exhibits hysteresis: when the deposit is returned to a lower temperature, the conductivity has increased because of the sintering that has occurred. To a first approximation, the conductivity is a function of only the temperature and degree of sintering, with the chemical composition of the deposit having little direct effect.

The algorithm to determine the degree of sintering, strength, and porosity of a deposit is based on the Frenkel equation (50), with an assumed value of surface tension. The equation is rearranged to yield a unitless time constant corresponding to an arbitrary degree of neck growth at a given viscosity. In practice, calculated viscosities for individual ash particles derived from CCSEM analysis are used. These are used to produce a mass-weighted average "unitless time" proportional to the expected degree of sintering, porosity, and strength. Further work is needed to obtain numerical coefficients relating the unitless time to actual time for a given degree of sintering to occur.

Experimental work will continue in this area in collaboration with Dr. Terry Wall of the University of Newcastle, New South Wales, Australia in the areas of deposit physical and optical properties. He will be visiting the EERC for a period of one month in February, 1994.

Doctoral Research Project

Mr. Bruce Folkedahl began a doctoral research program at the Pennsylvania State University. The focus of his research will be to develop a more effective slag viscosity model for higher-calcium coals such as the western U.S. types. The major tasks of his research project plan are as follows:

- Compile existing information relevant to predicting slag viscosity, specifically for high-calcium western coals.
- Obtain viscosity data for defined composition ranges of multicomponent slags in the operating regime of a rotating bob viscometer.
- Examine the feasibility of penetrometer viscosity measurements to extend the range of viscosity measurements outside the limits of a rotating bob viscometer.
- Model the viscosity behavior of high-calcium slags, including non-newtonian effects.

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TASK 3.0 ADVANCED POWER SYSTEMS

Subtask 3.2 Pressurized Combustion

INTRODUCTION

One of the overall goals of the U.S. Department of Energy (DOE) is the development of the technology necessary to provide for a secure, reliable, affordable, and environmentally sound source of energy. This is important in order to ensure economic stability and growth in the next century as well as to reduce current and minimize future environmental impacts associated with power generation in the United States and the world as a whole. The continued and potentially expanded use of abundant coal reserves is one key to a secure and affordable source of energy in the United States.

Throughout the world, coal will play an expanded role in the production of affordable energy necessary to meet the demands of economic development and growth. The development of more efficient and environmentally sound technology in the United States may present export market opportunities throughout the world; specific examples include East Central Europe and the Pacific Rim. In Eastern Europe, where substantial coal utilization has occurred for decades, an urgent need exists for commercial emissions control technology as well as for current clean coal technology. The lack of emission control technology in East Central Europe is exacting a high price in terms of human health and long-term environmental damage. In contrast, the Pacific Rim has only recently begun to expand the use of coal to meet energy demands motivated by economic growth. Therefore, the need in that region is for commercial and developing technologies to allow new coal-fired plants to meet current and future energy demands in an environmentally sound manner.

In order for coal to play a key role in the U.S. energy mix, it will be necessary to develop and commercialize technologies capable of producing electricity at significantly higher overall system efficiencies than the 30%–35% levels currently observed in conventional coal-fired systems. Also, the production of liquid and gaseous fuels from coal will be necessary in order to effectively meet the broad spectrum of future energy needs. In order to achieve overall system efficiencies of 40% to 60% in an environmentally acceptable manner, development and demonstration of advanced second-generation utilization and conversion technology will be necessary. Examples include 1) advanced pulverized coal-fired combustion systems; 2) high-temperature heat exchangers for indirect firing of gas turbines; 3) pressurized combustion in staged, entrained-, slagging, and fluidized-bed modes; and 4) integrated gasification and direct gas-fired turbines.

A number of barrier issues exist that are not unique to individual technologies but are in some manner common to all advanced power system processes for both oxidizing and reducing environments. Examples include materials issues, specifically ceramic and refractory components, and operational issues unique to high-temperature pressurized systems.

OBJECTIVES

The goal of the pressurized fluidized-bed combustion (PFBC) activity is to generate fundamental process information that will further the development of an economical and environmentally acceptable second-generation PFBC. The immediate objectives focus on generic issues, including the fate of alkali, the sulfide species in the carbonizer char, and the Resource Conservation and Recovery Act (RCRA) heavy metals in PFBC. A great deal of PFBC performance relates to the chemistry of the bed and the gas-solids contacting that occurs during combustion. These factors can be studied in a suitably designed bench-scale reactor. The present studies are focusing on the emission control strategies applying in the bed, rather than in hot-gas cleaning. Emissions include alkali and heavy metals in addition to SO_2 , NO_x , N_2O , and CO . No work was proposed on the pilot-scale carbonizer. However, some of the chemistry of the carbonizer was simulated in the small-scale reactor.

The goal of the research on slagging combustion reported here is to understand and predict the effect of low-rank coal properties on the design and operation of advance power systems. Barrier issues to be studied over time include slag rejection, sulfur capture, alkali partitioning, and slag corrosion. The objective of slag attack research is to mitigate slag corrosion of ceramic materials in a slagging coal-fired combustor.

ACCOMPLISHMENTS

Shakedown of Bench-scale Pressurized Fluidized-Bed Reactor

The first shakedown tests on the pressurized fluidized-bed reactor (PFBR) were conducted with no fuel feed. Three different sizes of silica sand were tested to determine how each behaved as bed material. These tests were performed at both atmospheric pressure and a pressure of 150 psia. A coarse size, -20 mesh, was chosen as the standard. Smaller sizes were found to blow out of the reactor to be collected in the cyclone pot. Another observation made during these early tests was that bed material tended to drop out of the reactor into the pot below at atmospheric pressure. As a result, the valve between the reactor and the bed material collection pot was kept closed during normal operation. It could be opened periodically during a run to examine bed material. During the course of testing, the feed delivery auger was prone to binding. A new auger was fabricated to alleviate the problem.

The data acquisition and control system has been streamlined and fine-tuned. The air and nitrogen flow rates are controlled automatically to flow rate set points. The reactor pressure is automatically controlled to a pressure set point. The three ceramic heaters on the reactor may be controlled manually to a given heater temperature or controlled automatically to maintain a desired gas temperature in each zone. Initially, it was hoped that the fuel auger speed could be controlled automatically to maintain a given excess air level in the bed; however, repeated attempts have shown that the lag time between a change in the auger speed and a change in the excess air was too great for this particular control loop to be effective.

The first test with fuel was conducted at atmospheric pressure with a delayed coke and a silica sand bed. This fuel was chosen because a supply of it was available in the desired size range. The control loops performed well.

The next combustion test was performed at atmospheric pressure with a fluid coke, Plum Run dolomite, and a silica sand bed. Nitrogen and air were both added to achieve the desired temperature, excess air level, and velocity. This fuel was very fine, and there was a high percentage of unburned carbon in the cyclone ash.

Blacksville bituminous coal was burned next, at atmospheric pressure and an average reactor temperature of 1550°F. Dolomite was added to achieve 90% sulfur capture.

The first shakedown test performed at pressure was performed with Blacksville coal and spent bed material from the TIDD station. The target conditions were 180 psia, 25% excess air, and 1565°F average bed temperature. Much more flue gas cooling is required at high pressure than at atmospheric to control the temperature of the flue gas going into the pressure letdown valve. A lot of plugging occurred during this test, first in the letdown valve, and then in the rest of the system.

The second shakedown test at pressure was also conducted with Blacksville and TIDD bed material, with the addition of Plum Run dolomite. Unlike atmospheric tests, where the drain valve at the bottom of the reactor was closed to keep material in the system, this valve remained open during the pressure test. No loss of bed material was observed; in fact, an increase of bed pressure drop suggested an accumulation of bed material. Sulfur capture was greater than 90%. The test proceeded smoothly until the cyclone plugged.

During the first shakedown tests, the temperature profile in the reactor was not as uniform as it should have been. The thermocouples in the reactor were relocated from being flush with the reactor wall to penetrating into the reactor about an inch. This configuration has yielded higher temperature measurements and a much more uniform temperature profile during the most recent shakedown test, performed at atmospheric pressure with Blacksville coal.

The reactor will be used to evaluate products from the Foster Wheeler Development Corporation (FWDC) second-generation carbonizer during the remainder of the program. A combustion test matrix will be selected based on input from FWDC.

Selection of In-Bed Alkali Gettering Materials

A literature search was conducted to develop a comprehensive list of alkali getting materials tested in other programs. Both oxidizing and reducing atmospheres were reviewed, since even in PFBC systems some of the initial alkali getting is likely to be occurring under localized reducing conditions. The various alkali getters investigated by these researchers (1-10) include the following:

- Diatomaceous earth (Celatom-MP-91)
- Activated bauxite
- Clay minerals

- Silica gel
- Burgess No. 10 pigment (kaolin clay)
- Silica gel, montmorillonite, kaolinite, bauxite, green limestone, Tymochtee limestone, alumina powder, Dolowhite
- Illite
- Bentonite and franconite (natural minerals based on montmorillonite)
- Sillimanite, feldspar, mullite, and kyanite (not very effective)
- Talcum, $\text{Mg}_6(\text{OH})_4\text{Si}_8\text{O}_{20}$ (effective to some extent)
- Calcium silicates
- Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$)
- Montmorillonite ($n(\text{Ca}, \text{Mg}) \text{O} \cdot \text{Al}_2\text{O}_2 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$)
- Halloysite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$) $n = 2$ to 4
- Allophane ($\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot n\text{H}_2\text{O}$)
- Sericite ($(\text{Na}, \text{K})_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$)
- Beidellite ($\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$)
- Pyrophyllite ($\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$)
- Illite ($(\text{K}_{1-15} \text{Al}_4(\text{Si}_{7-85} \text{Al}_{1-15}\text{O}_{20})(\text{OH})_4)$)
- Illite-Montmorillonite ($([\text{Na}, \text{Ca}]_{0.33} [\text{Al}, \text{Mg}]_2 \text{Si}_4\text{O}_{10}[\text{OH}]_2 \cdot n\text{H}_2\text{O})$)
- Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)
- Sillimanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)
- Alundum
- Attapulgous clay
- Novakite
- Emathlite/kaolinite/bauxite
- Vansil CaSiO_3
- Zeolite
- CaO impregnated in bauxite or kaolinite for SO_2 and alkali control

Alkali getters likely to be tested first in the PFBR would include the kaolinite, montmorillonite, illite, and activated bauxite materials. Kaolinite would be the first choice based on the literature and some previous research conducted at the EERC. In this research, kaolin was feed with a high-sodium, low-ash Spring Creek mine (Montana) subbituminous coal in a ratio of 1 part kaolin to two parts ASTM coal ash. These entrained flow alkali gettering tests were conducted in the pressurized drop-tube furnace (PDTF) at 1500°C and 100 psig with a two-second residence time. In these tests, over one-half of the total sodium was shifted to the larger fly ash particle sizes with the addition of the kaolin. This shift was indicative of a chemical reaction of the vapor-phase sodium with the kaolin to form sodium aluminosilicates. It would be interesting to try kaolin as a in-bed alkali getter in the PFBR. At lower temperatures, less of the alkali would be in the vapor phase, which should allow the kaolin to scavenge the alkali molecules more efficiently, and the longer residence time in a fluidized bed should improve kaolin performance. One concern would be the friability of the kaolin, which if too high would allow it to blow out the reactor before it had reacted significantly. Another concern would be that the sodium aluminosilicate formed would have a low melting point that might lead to bed agglomeration problems.

Corrosion of Monolithic Refractories

To achieve higher efficiencies in coal-fired power systems, higher temperatures of the working fluid within a heat exchanger are required. Several candidate alloys or

ceramics are available that will provide structural stability and chemical stability in air, although ceramics will be required for temperatures over about 980°C. Silicon carbide-based structural ceramics are targeted for the higher temperatures because of their high thermal conductivities and high strengths. Theoretically they should be stable to around 1430°C in a combustion environment. However, tests performed at the EERC under another project have shown that dense SiC is prone to slow, but unacceptable, corrosion by ash at temperatures over about 1200°C. Therefore, protective high-conductivity coatings such as SiC-based refractories are needed to prevent corrosion of the ceramic surface by coal slag. However, since the corrosion resistance of the refractories themselves was not known, this research was organized to measure corrosion resistance in commercially available refractories and to devise methods to reduce corrosion rates. We have focused on monolithic refractories because, compared to brick refractories, they are much cheaper, can be easily installed and replaced in the field, and maintain intimate contact with the heat exchanger so that heat transfer is as high as possible.

Background

Monolithic refractories are presently being used in coal combustion environments as replaceable, corrosion-resistant coatings on cooled surfaces such as those inside cyclone burners. Because they can be applied in thin layers and maintain intimate contact with the substrate, they have the potential to serve as inexpensive, high thermal conductivity corrosion-resistant coatings for heat exchangers. In particular, the silicon carbide (SiC)-based refractories have thermal conductivities superior to those of conventional materials such as alumina or chrome-based refractories. Much of the corrosion resistance of SiC-based monolithic refractories is because of their ability to conduct heat away from the slag and freeze a layer of slag next to the refractory. It was not known how they would perform in situations where the under surface is itself so hot that not enough heat can be conducted away and the slag therefore remains molten. For areas where heat transfer is not critical, alumina-based refractories may be applicable. Alumina monolithic refractories are known for their high-temperature stability and their resistance to thermal shock, but they had not been tested in the presence of coal slag.

In advanced coal combustion systems, working fluid temperatures may be much higher than in today's systems. The higher temperatures will raise the protective refractory above the slag melting temperature, preventing a layer of slag from freezing on and protecting the refractory. In order to determine the maximum use temperature for commercially available monolithic refractories, the interactions between refractories and coal ashes are a range of temperatures must be understood. Once the mechanisms of corrosion have been identified, methods to reduce corrosion, such as coal additives or materials improvements, can be investigated.

Previous corrosion experiments on SiC-based materials focused on structural ceramics (11, 12) and SiC refractory bricks (13). The corrosion of structural SiC ceramics by acidic coal slags at 1230°C resulted in localized corrosion by iron silicides (11). The corrosion by high-calcium, basic slags at 1240°C was a uniform dissolution of the protective SiO₂ layer by CaO in the slag to form calcium silicate compounds (12). The corrosion of SiC refractory bricks by acidic and basic slags at 1500°C involved the formation of iron silicides, and the basic slag corroded the SiC more rapidly than the acidic slag (13).

Although the literature describes corrosion of SiC ceramics and refractory bricks, little information exists on the corrosion of monolithic SiC refractories by coal ash. Monolithic refractories are nonbrick materials, usually mixed with water at the application site, applied to a surface in a cement-like form, and fired to sinter the material, causing it to develop strength. Monolithic refractories are more suitable for heat-exchanger coatings than for refractory bricks because they can be more easily applied by casting or gunning in any thickness and because they form a more intimate contact with a heat exchanger surface than with bricks. To ensure that monolithic refractories remain in place during firing, a low-temperature binder or cement is used. Two common binder materials are phosphoric acid, which produces a chemical bond at 260°C, and calcium aluminate, which develops a ceramic bond at 980°C.

To determine slag corrosion mechanisms and rates, several commercially available SiC refractories were subjected to static slag corrosion tests. They included both castable and plastic monolithic refractories donated by Carborundum Company, Harbison-Walker, and Premier Refractories. Much of the SiC refractory work was performed under the Combustion 2000 project for which the EERC is a subcontractor. The data from that research, summarized here, were presented at the American Chemical Society conference in Chicago, August, 1993 (14). The Combustion 2000 data are presented here for purposes of continuity with the Cooperative Agreement research on refractory corrosion. Under Cooperative Agreement funding, alumina monolithic refractories were also tested, and those results are included in this report. In addition, experimental SiC monolithic refractory binders were developed and tested for their corrosion resistance. Finally, methods of changing the corrosiveness of the slag were formulated and tested.

Experimental

These experiments focused on ash corrosion mechanisms and rates for castable and plastic monolithic SiC refractories. The castable materials contained calcium aluminate binders, and the plastics contained phosphoric acid binders. The SiC concentrations in the castables tested ranged from 75% to 83%, and the SiC concentrations in the plastics ranged from 59% to 71% (Table 3.2-1).

The samples were formed into cups to hold the coal ash during exposure. The samples were then prefired, causing vesicular glass coatings to develop on the plastics, but the calcium aluminate-bonded refractories were not affected, so the vesicular glass formation was attributed to the phosphoric acid binders in the plastic SiC refractories.

The two coal ashes used in the corrosion experiments included a high-calcium Powder River Basin (PRB) coal ash and a high-iron Illinois No. 6 ash (Table 3.2-2). Approximately 5 grams of ash was placed into the cup of each refractory sample, then the samples were heated to temperatures of 1093°C (2000°F), 1260°C (2300°F), and 1430°C (2600°F) at a rate of 120°C per hour. The castables were tested with both coal ashes at all exposure temperatures for exposure times of 40 to 80 hours. The plastics were tested only at 1430°C for an exposure time of 110 hours. All of the samples were quenched in air to determine phases present at temperature, then cross-sectioned and examined. The sample examination included optical microscopy and scanning electron microscopy with energy-dispersive x-ray analysis (SEM/EDX).

TABLE 3.2-1

Technical Data for the SiC Refractories

Material Name: Type:	SiC Castable 1	SiC Castable 2	SiC Plastic 1	SiC Plastic 2
Maximum Temperature,				
°C	1480	1482	NA	1593
°F	2700	2700	NA	2900
Composition, wt%				
SiC	83.0	75.1	70.6	58.6
SiO ₂	1.3	1.7	7.0	7.2
Al ₂ O ₃	12.5	19.0	18.6	29.6
CaO	2.8	3.4		0.1
Fe ₂ O ₃	0.2	0.5		0.2
P ₂ O ₅			3.4	4.0
Thermal Conductivity				
W/mK @1477K	5.8-8.7	4.23	6.2	4.96
Btu in./hr ft ² °F @2200°F	40-60	29.35	43.0	34.95
Density,				
g/cm ³	2.32	2.31	2.58	2.56
lb/ft ³	145	144	161	160

NA = not available.

Results and Discussion

SiC Castable Refractories

1093°C Exposure for 55 Hours

The two SiC castables, containing 75% and 83% SiC, were exposed to both ashes at 1093°C for 55 hours. After the exposure, the PRB ash was somewhat sintered, but porous and friable, and the Illinois No. 6 ash was well sintered and more dense than the PRB ash. Neither ash adhered well to the SiC refractory substrates, indicating that sootblowing would be an effective means of ash removal at this temperature. X-ray fluorescence of the ashes after the exposure showed that they did not react with the refractory, and there was no infiltration of the ash into the refractory.

1260°C Exposure for 45 Hours

PRB Coal Ash. Each castable sample contained a 3- to 4-mm layer of dark gray slag after the 1260°C exposure. The slag contained a few small vesicles indicating gas evolution during the exposure, and a continuous red reaction layer, 0.5 mm thick, was present at the undulating slag/refractory interface. The maximum depth of penetration of the slag into both refractories was 1 mm. Figure 3.2-1 shows several circular metallic phases, ranging up to 0.25 mm in diameter, at the interface. The circular nature of these phases, which were high in iron, indicated that they were liquid at 1260°C and immiscible with the slag. A few of the high-iron grains at the refractory/slag interface

TABLE 3.2-2

Compositions of the Coal Ashes Used in the Corrosion Experiments

Oxide	Powder River Basin Ash, wt%	Illinois No. 6 Ash, wt%
Na ₂ O	2.5	1.2
MgO	9.4	2.5
Al ₂ O ₃	15.9	18.5
SiO ₂	31.1	57.8
P ₂ O ₅	1.8	0.0
SO ₃	0.0	0.0
K ₂ O	0.3	0.6
CaO	33.0	3.7
TiO ₂	1.0	1.0
FeO	4.4	14.6
Base/Acid	1.0	0.3

$$\text{Base/Acid} = (\text{FeO} + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2).$$

contained 55 wt% Fe and 40 wt% O, but several other grains contained 60 wt% Fe, 10 wt% Si, 20 wt% P, a composition similar to that of the iron silicides described in other studies (11, 12). Iron silicides are stable only under reducing conditions, and their presence indicates that portions of the slags had low partial pressures of oxygen during the exposure. The iron oxide in the slag reacts with the SiC to form the iron silicide, and this reaction also causes gas evolution of CO or CO₂.

The remaining slags in both samples contained less calcium oxide and more silica than the original ash (Table 3.2-2). The decrease in calcium is difficult to explain, because no high-calcium phases were identified, but the increase in silica can be explained by the oxidation and dissolution of SiC grains from the refractory into the slag.

Illinois No. 6 Coal Ash. The slags remaining in the castable samples ranged from 5 to 6 mm thick and were black in color. Many vesicles were present in the slag, indicating gas evolution during the exposure. The samples exposed to the PRB ash contained only a few vesicles, indicating that the refractory reacted less with the PRB ash to produce fewer vesicles or that the PRB slag was less viscous at this temperature, as indicated by laboratory viscosity measurements, and allowed vesicles that formed to escape rapidly from the slag.

The maximum depth of corrosion reached 0.25 mm, but corrosion and surface pitting of the refractories were uneven and occurred in isolated areas, unlike the samples exposed to the PRB ash, which had even reaction layers. The slag/refractory interfaces in the samples exposed to the Illinois No. 6 slag contained discontinuous red reaction layers and circular, iron-rich phases, 0.25 to 0.5 mm in diameter (Figure 3.2-2). The iron phases were composed of 75–80 wt% Fe and 15–20 wt% Si, with little or no O or P. The formation of the silicide phases resulted in a slag composition which differed slightly from the original ash composition. The slag contained less iron oxide than the original ash, but no changes occurred in the concentrations of the other major oxides.

Figure 3.2-1. SEM micrograph of the reaction layer between the slag and a SiC castable refractory exposed to a PRB coal ash at 1260°C for 45 hours.

1430°C Exposure for 40–80 Hours

PRB Coal Ash. The residual slag layers in the castable SiC refractories ranged from 1 to 3 mm thick after the 1430°C exposure. The slag was able to penetrate 2.5 mm into the refractory materials, and the penetration was aided by dissolution of the refractory binder and the incorporation of SiC grains into the slag. Some of these incorporated SiC grains were coated with reddish iron silicides, indicating that the iron in the slag was reduced to elemental iron and reacted with the SiC to produce iron silicides. Only a few circular iron silicides were present in the slag and ranged from 0.25 to 1.0 mm in diameter. The average composition of the silicides was 70 wt% Fe, 10 wt% Si, and 10 wt% P. The samples exposed to the PRB slag at 1430°C for 80 hours showed similar results. The maximum depth of slag penetration was 4 mm for the 80-hour samples, which is about twice the depth of penetration for the samples exposed for 40 hours.

The remaining slag contained less calcium and magnesium and more silica than the original ash (Table 3.2-2). The increase in silica content resulted from oxidation and dissolution of SiC grains by the slag. The decrease in calcium, which was also observed for the 1260°C exposure, is not well understood but may be related to the formation of a calcium-rich phase not observed.

Illinois No. 6 Coal Ash. The castable SiC samples contained layers of vesicular slag that ranged from 3 to 5 mm thick. Several circular metallic grains, approximately 0.25 to 0.5 mm in diameter, were present at the undulating refractory/slag interfaces. These grains containing 75 wt% Fe, 20 wt% Si, 5 wt% O₂, and less than 2 wt% P were

Figure 3.2-2. SEM micrograph of the slag/refractory boundary in a SiC castable refractory exposed to an Illinois No. 6 coal ash at 1260°C for 45 hours.

present in isolated areas along the slag/refractory interface. The maximum depth of slag penetration was 0.75 mm for 40 hours and 3 mm for 80 hours.

The castables seemed to react less with the Illinois No. 6 ash than the PRB ash, but some reaction occurred to alter the slag composition. The resultant slag contained less iron and more calcium and silica than the original ash. The reduction of iron in the slag resulted from the formation of iron silicides during the dissolution of the SiC refractory.

SiC Plastic Refractories

1430°C Exposure for 110 Hours

PRB Coal Ash. Three plastic refractories, with SiC compositions ranging from 58% to 70%, were exposed to the PRB ash at 1430°C for 110 hours. After exposure, the samples were quenched, cross-sectioned, and examined optically. The plastic samples contained residual slag layers 3 to 4 mm thick; a few iron silicides, 0.5 to 1.0 mm in diameter, were present in the slags. The slag easily penetrated the plastic refractory materials, and penetration depths reached 10 mm in most samples, indicating the high porosity of the plastics. More slag penetration would be expected in a dynamic corrosion setting with slag replenishment.

Conclusions for SiC Refractories

Figure 3.2-3 illustrates the penetration rates for castable refractories exposed to the PRB and the Illinois No. 6 ashes in the static corrosion tests. The 1093°C exposure, which showed no ash penetration, was not included in the table, and the plastics were omitted because of their rapid penetration rates. In general, the PRB ash was more corrosive for all exposures. A dramatic increase in the corrosion rate occurred from the 1260°C to the 1430°C exposure for the PRB ash. The corrosion rate of the Illinois No. 6 ash also shows an increase from the lower to the higher temperature, although the increase is not as dramatic.

The differences in penetration rates of the two coal ashes may be related to slag viscosity, which is dependent on ash composition and temperature. The base-to-acid ratios indicate that the PRB slag probably had a lower viscosity at all exposure temperatures, which would facilitate the diffusion of corrosive elements (Ca and Fe) to the SiC surface. As temperature increases, viscosity decreases, increasing diffusion. The penetration rates also increased when the exposure time was increased from 40 to 80 hours at 1430°C. In general, the PRB slag was more corrosive, and increasing temperature and exposure time caused increases in corrosion rates.

It should be cautioned that these penetration rates are derived from static slag corrosion tests and do not take into consideration erosional effects of flowing slag or replenishment of fresh slag in a dynamic system. In a dynamic system, penetration rates are expected to be higher than rates determined from these static tests, but these results are still useful for comparison purposes.

Figure 3.2-3. Penetration rates of the SiC castable refractories exposed to PRB and Illinois No. 6 ashes.

Alumina-Based Refractories

Several alumina-based monolithic refractories were subjected to similar slag corrosion testing. These materials were also donated by Carborundum Company and Premier Refractories, and included two high-alumina castables, Alumina 1 (96% Al_2O_3) and Alumina 2 (97% Al_2O_3) (Carborundum and Premier Refractories), and an alumina-silica or mullite castable (67% Al_2O_3 and 25% SiO_2) from Premier. The refractories were exposed to the PRB ash and the Illinois No. 6 ash at 1430°C for exposure times ranging from 50 to 155 hours.

In general, the alumina-based refractories showed extensive slag infiltration and reaction at 1430°C. The refractory surfaces were porous, which enhanced slag penetration and reaction. The penetration rates for the Illinois No. 6 ash were higher for both the Alumina 1 and 2 refractories (Figure 3.2-4). The penetration rates for the mullite refractory were high for both ashes, and the sample exposed to the PRB ash collapsed when it was removed from the furnace, which indicates that this refractory may have a tendency to spall in a real system when exposed to this type of ash.

The differences in penetration rates of the two coal ashes is probably related to reactions between the alumina in the high-alumina refractories and the coal ashes. Interactions between the slags and refractory may alter the original slag viscosities, possibly making the PRB ash more viscous than the Illinois No. 6 ash at the exposure temperature. Viscosity measurements indicated that the PRB slag has a lower viscosity than the Illinois No. 6 slag at the exposure temperature, but additions of alumina into the PRB slag may have altered the viscosity, possibly by causing crystallization. No SEM/EDX data are available at this time to verify this conclusion.

Development of High-Temperature Corrosion-Resistant Binders for Monolithic SiC Refractories

Background

The binder or matrix material for a monolithic refractory must provide low-temperature strength so that the refractory holds its position while firing and must fire into a matrix that holds the refractory grains together without spalling or crumbling. Also, the firing temperature must not be so high as to be unreachable safely in the system in which the refractory is employed. These requirements are met in most commercially available monolithic refractories by calcium aluminate or phosphoric acid-type binders. However, these binders were shown in the experiments described above to be prone to coal slag corrosion at temperatures of 1200°C and above. Therefore, we chose two tactics in designing new binders that could impart corrosion resistance to monolithic refractories at higher temperatures. The first was to develop a binder inherently corrosion-resistant. This work was funded under the Combustion 2000 project for which the EERC subcontracted to the United Technologies Research Center (UTRC). The work was successful in developing a monolithic refractory binder that increased the lifetime of the fired material by a factor of ten when the refractory was exposed to bituminous coal slag at 1430°C. That work is reported in the Combustion 2000 quarterly reports for the UTRC effort.

Figure 3.2-4. Penetration rates for the alumina-based refractories exposed to PRB and Illinois No. 6 ashes.

The second approach to imparting corrosion resistance to slag was to design the binder to interact with the slag, partially dissolving in it, and raising the solidus temperature of the mixture enough to force it to freeze next to the refractory surface. That research was funded under the Cooperative Agreement and is reported here. Although many different formulations were tested, only tests with the last formulation are described, since they represent the accumulated experience and most up-to-date results for the experimentation.

Experimental

High-calcium coal slags, such as those produced from Powder River Basin (PRB) coals were shown in the experiments reported above to be much more corrosive than low-calcium bituminous coal slags to commercially available monolithic refractories. Therefore, we focused the experimental binder research on the same PRB ash used for the commercial refractory corrosion tests described earlier in this report. The Al_2O_3 -CaO-MgO-SiO₂ ceramic system is the one that most closely represents the composition of PRB ash and for which the most thermochemical equilibrium data is also available. As shown in Table 3.2-2, no oxide other than these four makes up more than 5% of the slag. The composition of the PRB slag is plotted on the ternary diagram shown in Figure 3.2-5 (19) as point A. The ternary represents a section of the system taken at a constant level of 15% Al_2O_3 . A material with that composition would have a solidus in the range of 1225°–1285°C (20). This is nearly the lowest possible solidus temperature in this system. However, shifting the composition toward the MgO apex can increase both solidus and

Figure 3.2-5. The CaO-MgO-SiO₂ ternary at a constant 15% Al₂O₃ level. Point A = PRB coal ash, Point B = high-solidus composition, Point C = experimental binder composition.

liquidus temperatures substantially. Therefore, if a binder rich in MgO dissolved into the slag, the solidus temperature of the slag could be raised enough to freeze the slag next to the refractory. A shift in composition to point B in the figure would increase the solidus (freezing) temperature of the slag to approximately 1400°C.

To be a good binder for a monolithic refractory, the material must provide low-temperature strength as well as specific high-temperature properties. As describe earlier in this report, the phosphoric acid-based binders exhibit poor corrosion resistance, so we decided to design the binder to be a hydraulic cement. Unfortunately, MgO does not make a good cementitious material, so it had to be mixed with a calcium silicate or calcium aluminate, which are cementitious. In order to impart good high-temperature strength to the binder, the materials were mixed in a proportion that itself has the highest solidus temperature possible. A search of the available data showed that the highest solidus temperature achievable for a MgO-CaO-(Al₂O₃ or SiO₂) system is around 1400°C. Point C in Figure 3.2-5 is a composition with this solidus temperature that would shift the composition of the slag to point B when dissolved in the slag at a 50:50 ratio.

The material was prepared by mixing reagent-grade oxides in a platinum crucible, heating to 1700°C for 4 hours, and quenching by pouring directly into water. Since the liquidus temperature of the material is 1950°C, a small amount of crystalline periclase (MgO) remained undissolved. Water quench was preferred to quenching on brass because it fractured the material, making grinding easy, and because it may form some hydroxide groups, making it a better cementitious material. After quenching, the material was

dried at 100°C and ground to -600 mesh. It was then mixed with 37 Crystollon, a refractory-grade silicon carbide donated by Norton. Mixing ratios were 5% and 15% experimental binder by weight. After shaking the binder and SiC together, enough water was added to just wet the binder, making a relatively dry mud-like mixture. Typically 5%-8% water was added by weight. The wet mixture was packed into a cylindrical mold 1½ in. in diameter, and a steel rod was used to create a central well ½ in. in diameter by ½ in. deep. The rod was lightly vibrated into place, which brought a slight excess of binder to the surface of the well. After overnight curing, the refractory was heated to 1450°C at 5°C/minute, held for 10 hours to fire it, then cooled to room temperature at 5°C/minute. PRB ash was then packed into the well. The refractory cylinder was heated at 10°C/min to 900°C, then 2°C/min to 1100°C to allow SO₂ to evolve from the sulfates without excessive foaming, then to 1380°C and held for 80 hours. After cooling at 10°C/min, the cylinders were sectioned with a diamond water saw and observed in an optical microscope.

Results and Discussion

As with the commercial refractories, the slag had strongly wetted the silicon carbide and most of the slag had climbed out of the well, over the refractory cylinder, and down onto the substrate. The slag remaining in the well was white, most likely because it contained microcrystalline material. When commercially available refractories are tested, the remaining slag is always clear (glassy), so the white appearance of the slag in the test refractory well indicates that interaction with the refractory had caused some crystallization. The slag that had completely overflowed onto the substrate was still clear, indicating that it had not remained in contact with the refractory long enough for crystallization to be induced. Some dissolution of the binder was evident because SiC crystals often projected above the surface of the well and into the slag, although slag penetration into the body of the refractory was much less than seen in the commercial refractories. However, the cylinder made with only 5% binder was deeply cracked circumferentially, showing that 5% binder provides insufficient strength to the material. One cross section of the 15% binder material was coated with carbon and viewed with a scanning electron microscope and energy dispersive x-ray analysis (SEM/EDX) was used to measure changes in composition of the slag. Table 3.2-3 shows the composition of the experimental binder, the coal slag, and averages of three areas exposed at the cross section of the slag remaining in the well and the slag that had flowed up and out of the well down to the substrate. The three spots used in the averages for each of the two types of slag had very similar compositions.

The protruding SiC crystals with relatively little change in MgO from the original ash to the slag implies that a small amount the binder dissolved in the ash and was diluted back to the original concentration by the increase in SiO₂. The decrease in calcium in the slag has occurred for all tests of the PRB ash in all SiC monolithic refractories. The loss of the Ca has never been fully explained, but it is assumed that calcium-rich crystalline material formed that removed the calcium from the liquid. However, these crystals are not visible in the backscattered electron imaging mode in the SEM, so they are either sporadic and submicron, or they have nearly the same atomic number as the remaining slag. Some of the MgO may also have been trapped in these crystals along with the missing alumina in the internal slag, possibly indicating the formation of (Ca,Mg) alumina spinels. The large increase in SiO₂ in both internal and external slag shows that the refractory-grade SiC had dissolved in the slag, most likely by

oxidizing to SiO_2 , then dissolving into the slag. Because the slag had climbed out of the refractory, the slag layer was thin, and oxygen transport could be relatively rapid. No SiO_2 layer remained at the interface between the slag and the SiC, indicating that it dissolved as rapidly as it formed. The loss of refractory was only about one half that of the best commercially available refractory, although the commercial material was tested at 40°C higher. Even so, we believe that the experimental binders show enough promise to warrant further investigation, especially under conditions where the slag cannot flow away from the refractory.

Conclusions of the Experimental Binder Testing

The experimental binder was successful in causing crystallization in the slag and in reducing the overall oxidation of the SiC in the refractory as compared to the best commercial SiC monolithic refractory tested so far. However, the PRB ash strongly wets the refractory and flows out of the slag well, leaving a thin liquid layer. Also, since the SiO_2 layer that normally forms on the SiC during passive oxidation dissolves into the remaining slag, the SiC is then subjected to relatively rapid active oxidation. However, O_2 transport would be slowed considerably if the slag remained as a layer on the refractory, as it would in a real-life situation. Therefore, we suggest further testing under conditions where the slag is either continually replaced or not allowed to flow away from the refractory.

Coal Additives for Corrosion Prevention

Background

From the laboratory experiments, several possible corrosion mechanisms have been identified for SiC-based materials. The high-calcium PRB ashes have the potential to dissolve the protective SiO_2 layer that forms on the surface of SiC, which exposes the underlying SiC surface to corrosive slag species, such as iron. The PRB ashes also dissolve refractory binders, which allows the incorporation of SiC grains into the slag. In the case of the Illinois No. 6 slag, the iron in the slag directly attacks the SiC to form iron silicide phases. Several coal additives have the potential to reduce the corrosiveness of slags in contact with ceramics and refractories.

A literature survey was conducted to identify commercially available coal additives used in combustion systems. Several common additives used for altering ash and slag

TABLE 3.2-3

Normalized Compositions of the Experimental Binder, Original Slag,
and Remaining Internal and External Slag, wt%

	Binder	Ash	Internal Slag	External Slag
MgO	31	11	10	10
CaO	29	37	18	11
SiO_2	25	35	67	62
Al_2O_3	15	18	5	18

properties include copper oxychloride, limestone, dolomite, and clay minerals (21). Although the literature presents some of these additives for corrosion prevention, most are used to lower ash fusion temperatures to generate a fluid slag. Lowering slag viscosity may increase corrosion of ceramics in contact with the slag. One additive, copper oxychloride, can increase the crystallization rate in a slag with only small additions, which may be useful in corrosion prevention.

Copper oxychloride ($\text{Cu}_2(\text{OH})_3\text{Cl}$) was developed in the 1960s as a coal additive to mitigate slagging problems (22). This compound is added to the coal in small doses (5–10 ppm), unlike most additives, which are added in quantities of a few weight percent to change the ash composition. The combustion products of copper oxychloride, $\text{CuO}/\text{Cu}(\text{OH})_2/\text{Cu}$ and $(\text{CuCl})_n$, have been shown to transform dense deposits into porous, friable deposits by promoting crystallization in slags (22). The combustion products from the copper phases are dispersed in the vapor phase during the combustion of the coal, and condense and react on the surfaces of the deposits.

Kiss and others (23) suggest that the copper oxide compounds are reduced by FeO in the slag to produce metallic copper, which provides nucleation sites for crystallization. The ability of copper to oxidize ferrous iron may be useful to prevent corrosion of ceramics in contact with coal slags. Iron in coal slags has been found to attack SiC ceramics rapidly (21). The reaction occurs by the reduction of iron oxides in the slag by SiC, which results in the formation of iron silicides and CO or CO_2 . If the presence of copper promotes oxidation, then metallic iron would be less likely to form and react with the SiC.

Copper also promotes crystallization of spinel phases, such as hercynite ($\text{Fe}^{+2}\text{Al}_2\text{O}_4$) (23). The formation of hercynite would lock the iron in a stable phase and render it unable to react with the SiC. The removal of the iron from the slag and the crystal formation would increase slag viscosity, and this would decrease the migration of corrosive species to the ceramic surface.

A laboratory experiment was conducted to determine the effects of copper oxide additions on crystallization of a high-iron Illinois No. 6 slag. A small addition of CuO (1 wt%) was added to the ash. The ash and copper mixture was heated to 1400°C for 30 minutes, then quenched. The slag was examined with SEM/EDX. The SEM revealed a high concentration of blocky crystals, 5 μm in diameter, in the slag (Figure 3.2-6). Analyses indicated that iron and oxygen were the main elements present in the crystals, which were probably magnetite (Fe_3O_4). The formation of these crystals may influence the slag corrosion of SiC ceramics by increasing slag viscosity. The presence of crystals increases frictional forces and thus increases the viscosity of the slag. Also, magnetite formation would reduce the amount of iron in the residual slag, which would increase the viscosity of the residual melt. The crystal formation ties up the iron, which is a major player in SiC corrosion, in a stable phase. This may reduce the mobility and availability of iron to react with SiC.

Slag Viscosity Modifications

Altering slag viscosity may aid in corrosion prevention of ceramics in contact with coal slags. Either decreasing slag viscosity or increasing slag viscosity may provide a means to protect the ceramic surface. In an oxidizing atmosphere, a thin layer of SiO_2 that can act as a protective coating forms on the surface of SiC. This layer can dissolve

Figure 3.2-6. SEM photo showing iron oxide crystals formed in the Illinois No. 6 slag with a 1 wt% copper oxide addition.

into the slag, leaving the SiC exposed directly to the slag. The preferred surface is the one that dissolves most slowly. The formation of the SiO_2 depends on the partial pressure of oxygen at the ceramic surface, which can be influenced by the thickness of the slag layer (12). A thick, viscous slag layer would not allow as rapid oxygen penetration to the ceramic surface, and the diffusion of oxygen would be impeded by the formation of bridging oxygens in the melt. But a viscous slag would be more erosive than a fluid slag because of the shear stress on the surface of the ceramic. Also, the diffusion rates of corrosive ions to the SiC surface are much slower in a slag with higher viscosity and fewer nonbridging oxygens. Therefore, the migration of corrosive species, such as iron, would be impeded. Therefore, increasing slag viscosity seems to be a plausible method to reduce slag corrosiveness of low viscosity slags, such as the high-calcium PRB slags used in these experiments.

Calcium

Limestone is commonly used as a calcium additive to coals to reduce slag viscosity (21). But limestone additives have also been shown to increase the viscosity of molten ash deposits, which decreases the deposit's ability to sinter and develop strength (24). The different effects of calcium additions are related to the type of coal fired, as well as operating conditions. The ternary phase diagram of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ systems indicates that in low-calcium coals, the addition of CaO would reduce the liquidus temperature (25). With high-calcium coals, additions of CaO would increase the liquidus temperature. These predictions are based on simple ternary systems and do not consider the effects of small amounts of fluxing agents, such as sodium or iron, on the liquidus

temperature of the melt. Experiments are proposed, in the continuation of this project, to determine the effects of calcium additions on slag viscosity.

Aluminosilicates

Clay sediments usually contain abundant clay minerals, such as kaolinite. Kaolinite is a hydrous aluminosilicate ($\text{Al}_2\text{Si}_2\text{O}_5[\text{OH}]_2$) which forms fine particles in sedimentary rocks. Because of relatively high alumina-to-silica ratio, kaolinite has the ability to increase the liquidus temperature of some deposits, which reduces deposition problems (21). This may aid in corrosion prevention on a ceramic surface. The formation of a viscous slag layer on the ceramic may impede the migration of corrosive species to the ceramic surface. This protective layer could be maintained by intermittent pulsing of the additive to produce the viscous layer. The pulsing would allow a thin protective layer to form, but would not allow the buildup of thick deposits because the pulses would be intermittent. The bulk of the slag would be less viscous and flow freely over the "frozen" slag layer.

Pure systems of $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ have been investigated to determine the effects of oxide concentrations on viscosity (26, 27). The interest in this project is for systems with SiO_2 concentrations near 45%, which is the SiO_2 content of the PRB ash investigated in the corrosion studies. The temperature range of interest is 1400°C and above, which is the ceramic surface temperature expected in advanced power systems. In a pure system of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, with no MgO , at 1400°C , increasing concentrations of CaO result in decreasing viscosities (Figure 3.2-7) (26). In a system with MgO as the fourth major constituent, both increasing MgO and CaO concentrations cause a decrease in the viscosity of the bulk melt at 1400°C (Figure 3.2-8) (27).

The points plotted on Figures 3.2-7 and 3.2-8 indicate the composition of the Wyodak ash that was used in the corrosion experiments. Laboratory measurements of the viscosity of this ash indicate that above 1200°C , the slag is quite fluid (Figure 3.2-9). The corrosion studies indicate that this slag is corrosive at 1400°C , and the corrosiveness is facilitated by low viscosity. Figures 3.2-7 and 3.2-8 indicate that by increasing the SiO_2 and Al_2O_3 concentrations of the ash, the viscosity of the melt would increase at 1400°C . Additions of kaolin, silica, or a mixture of the two constituents would change the composition of the ash in a trend perpendicular to the viscosity contours and in the direction of increasing viscosity. Because coal slags are multicomponent systems, it is difficult to use 3- or 4-component systems, such as those represented in Figures 3.2-7 and 3.2-8, to predict viscosity changes. However, the major components are represented in the diagrams and indicate that increases in SiO_2 and Al_2O_3 will increase the viscosity of the slag. Experiments are proposed in the continuation of this project to determine the effects of kaolin and silica additions on the viscosity of the Wyodak slag. Because conditions at the slag/ceramic interface may be reducing, viscosity measurements should be performed in both oxidizing and reducing atmospheres.

The Development of a New Method of Calculating Coal Slag Viscosity

A new approach has been developed for the prediction of coal slag viscosity in the case of phase separation below the temperature of critical viscosity. This phenomenon causes deviations from ideal viscosity as compared to unseparated slag of the same bulk composition. The new method of viscosity calculation accounts for the structural changes

Figure 3.2-7. Viscosity contours of the CaO-Al₂O₃-SiO₂ system at 1400°C. The plotted point at 47 wt% SiO₂, 22 wt% Al₂O₃, and 31 wt% CaO indicates the Wyodak ash composition (Modified from Machin and Yee, 1948 [26]).

Figure 3.2-8. Viscosity contours of the CaO-Al₂O₃-SiO₂-MgO system at 1400°C and 45 wt% SiO₂. The plotted point at 20 wt% Al₂O₃, 27 wt% CaO, 8 wt% MgO (and 45 wt% SiO₂) indicates the Wyodak ash composition (Modified from Machin et al., 1952 [27]).

Figure 3.2-9. A plot of viscosity versus temperature for Wyodak in air.

in the slag as phase separation begins, assuming that viscosity depends on the degree of polymerization of the slag and the dispersion of nuclei. Arrhenian and configurational entropy models were combined to provide more accurate predictions of coal slag viscosity at temperatures below the critical temperature. The results of this work were presented at the Engineering Foundation Conference on the Impact of Ash Deposition on Coal-Fired Plants in Birmingham, UK, June 1993 and in the journal *Energy and Fuels*. The papers are included as Appendix 3.2-1.

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TASK 3.0 ADVANCED POWER SYSTEMS

Subtask 3.3 Catalytic Gasification

INTRODUCTION

Fuel cell technology is advancing rapidly, and a critical requirement for its application is economical hydrogen production. Coal gasification is a potential source of the hydrogen to feed the cell, provided the gas can be adequately produced and cleaned up at a reasonable cost. An expressed interest in gasifying bituminous coal resulted in its inclusion in tests currently being carried out at the EERC under the DOE-funded Catalytic Gasification project. The first part of this project involved catalyst testing with bituminous coal. It was followed with testing of lignite coal.

OBJECTIVES

Work on catalytic gasification was in direct support of efforts to integrate gasification and molten carbonate fuel cells. The primary goal was to identify a suitable hydrogasification catalyst to achieve coal residence times in the order of minutes in a gasifier operating first on bituminous and then on naturally reactive low-rank coal at nominal conditions of 650°C and 500 psi. Studies included evaluation of methods of catalyst application and composition.

ACCOMPLISHMENTS

Gasification Equilibrium Program

A program was developed that computes the equilibrium gas composition and heat balance for gasification of coal by steam, oxygen, and/or hydrogen. The program can be used to compare experimentally observed product gas compositions with equilibrium values and to estimate gas compositions for engineering systems analysis.

Equilibrium conditions are satisfied for the following:

- Steam gasification $C + H_2O = CO + H_2$, with the activity of carbon assumed to be 1.
- Water-gas shift $CO + H_2O = CO_2 + H_2$
- Methanation $CO + 3H_2 = CH_4 + H_2O$

The heat balance includes enthalpies for input and output streams and heat loss.

The program computes values of equilibrium constants and enthalpies as a function of temperature alone, based on data from the National Bureau of Standards, assuming perfect gas behavior.

Input streams to the gasifier include 1) coal, 2) steam, 3) oxygen, and 4) recycle gas. The product gas stream from the gasifier includes CO, CO₂, H₂O, H₂, and CH₄. The current version of the program uses an abbreviated elemental analysis for coal consisting of C, H, O, and ash, corrected to a total of 100%. The N and S in the coal are neglected, and no provision is made for treating a gas diluent such as air nitrogen in the input streams. The structure of the program is sufficiently general to add such components.

The method of solution used in the program is an n-dimensional Newton-Raphson iteration procedure applied to nonlinear equations for elemental (C, O, H) balances, the enthalpy balance, equilibrium relationships, and mole balance constraints. The method operates by inverting the augmented matrix of these equations and their partial derivatives to compute incremental changes leading to a solution. The solution vector includes eight variables: product gas compositions for CO, CO₂, H₂O, H₂, and CH₄; total moles of product gas; the steam rate required to satisfy equilibrium; and, alternatively, at the choice of the user, either the oxygen feed rate or the heat loss required to satisfy the enthalpy balance. The user may also specify computational control parameters to be used in place of the default values provided in the program. The program has been applied to a variety of conditions, including steam-oxygen and hydrogasification, and has indicated generally good convergence behavior over a range of temperatures, pressures, and reactant compositions. Failure to converge, or convergence to unreal negative solutions, may occur either because of instability in the conversion method or specification of input conditions for which there are no useful equilibrium solutions. The modular design of the program allows more powerful convergence methods to be substituted for Newton-Raphson without great difficulty.

The equilibrium program is written in Quick BASIC™ and is available in program code and compiled versions. Operation of the program is menu-driven, and allows the user to change a screen of preassigned input values for gasifier pressure and temperature, reactant inlet temperatures, coal analysis, gas recycle rate and composition, carbon conversion, and either heat loss or oxygen rate when they are not computed.

The gasification equilibrium program has also been incorporated into a Lotus 1-2-3 spreadsheet. In this version, a Lotus macro transfers a column of input data to an input/output file and automatically executes the compiled version of the equilibrium program. The solution vector is then transferred back to the Lotus spreadsheet. With slight modification, this version can be programmed to perform a series of equilibrium calculations for a range of gasification conditions.

As an outgrowth of this programming activity, an additional spreadsheet has been developed to compute molar enthalpies as a function of temperature for dry coal in relation to elemental analysis (C, H, O, N, and S), coal ash, and a number of gaseous, liquid, and solid reactants and products of interest in gasification and combustion systems. An integrated version of this spreadsheet incorporates these calculations, under macro control, into a general heat and material balance for coal conversion systems. The calculations are set up for up to four input streams and two output streams, with provision for redefining streams. The spreadsheet calculates error terms for the mass balance, the mole balances for C, H, and O, and the enthalpy balance. The spreadsheet can be used to zero out any one of these errors by automatically adjusting an appropriately selected stream flow, composition, or temperature through the use of error minimization macros which are simple numerical versions of the Newton-Raphson

method. This spreadsheet is a powerful tool for performing trial-and-error corrections in heat and material balances and allows a knowledgeable user to make motivated corrections that systematically zero out all of the computed error terms. The spreadsheet has been used to estimate exit gas temperatures for the gasification of coals of different rank and moisture content, showing good trend agreement with experimental data from the literature. Higher heating values calculated from enthalpies for 13 types of coal, from bituminous to lignitic and brown coal rank, differed from averaged experimental values by a standard error of 1.4%, compared to 1.8% for the DuLong formula. For northern Great Plains lignite and subbituminous coal and Australian brown coal, the standard error for heating values calculated by the enthalpy spreadsheet was only 0.5%, compared to 2.1% for the DuLong calculation.

Coal

Catalyzed steam gasification of Illinois No. 6 bituminous coal from the River King mine was investigated by two methods. The proximate analyses of the raw coal and coal containing approximately 10% added nickel are shown in Table 3.3-1. The initial tests were carried out by thermogravimetric analysis (TGA). Catalyst screening was accomplished by comparing the kinetics of the reaction between uncatalyzed feed and steam with the kinetics of the catalyzed reaction. Those materials illustrating greatest rate enhancement by TGA and potential for reuse were selected for larger-scale testing in the integrated bench-scale gasifier (IBG). Similar tests were carried out with Center, ND, lignite. The proximate analyses of the raw lignite and the lignite containing catalyst are shown in Table 3.3-2.

TABLE 3.3-1

Proximate Analyses of Illinois No. 6 Coal and Coal + 10% Ni Catalyst

	Moisture	Volatiles	Fixed Carbon	Ash
Raw Illinois No. 6	9.9	34.0	45.3	10.8
Raw Illinois No. 6 + 10% Added Nickel	--	37.8	50.2	12.0
Raw + Catalyst	5.1	17.6	23.5	53.8
Raw + Catalyst + 10% Added Nickel	--	18.6	24.7	56.7

TABLE 3.3-2

Proximate Analyses of Center Lignite and CL¹ with Ni and Fe Catalysts

	Moisture	Volatiles	Fixed Carbon	Ash
Raw CL	31.3	30.6	32.3	5.8
"	-	44.5	47.0	8.5
Raw + Ni	18.9	26.9	23.6	30.6
"	-	33.2	29.1	37.7
Raw + Fe	6.0	46.2	31.7	16.1
"	-	49.2	33.7	17.2
Raw + Fe-Ca	17.3	40.2	26.1	16.4
"	-	48.6	31.6	19.8

¹CL = Center Lignite

Catalysts

Potassium carbonate and nickel acetate were tested as catalysts with Illinois No. 6. Several methods of application of the catalyst to the coal were tested, including dry mixing and aqueous impregnation, where the impregnation was followed by either draining the excess liquid or drying under vacuum. Neither potassium carbonate nor nickel acetate is likely to be economically feasible for use as a catalyst for gasification, but they were included as baseline catalysts. Nickel-substituted synthetic mica montmorillonite clay (NiSMM) and iron-aluminosilicate clay prepared at the EERC (1, 2) were applied by dry mixing or introduced into the reactor prior to introduction of the coal. The catalyst was applied to the coal such that the catalytic metal was about 10% of the coal weight.

Catalysts tested with Center lignite were nickel nitrate and iron nitrate applied by ion-exchange, iron (2, 3) and iron-calcium compounds applied by insipient wetness, and nickel and nickel-molybdenum clays applied by dry mixing.

Catalyst Preparation

Preparation of Nickel-Substituted Synthetic Mica Montmorillonite (NiSMM)

Sodium silicate solution, 112 g, (27 wt% SiO_2), was dispersed in 1200 mL of deionized water. The sodium silicate solution was exchanged three times with Amberlite IR 120-H cation resin. Next, 81 g of nickel acetate tetrahydrate dissolved in 600 mL of water was added with stirring to the silica dispersion. Then 75 g of aluminum isopropylate and 2.4 g of ammonium fluoride were added with stirring. The resulting slurry was evaporated to remove some water, until the volume was to about one third. Sixteen milliliters of aqueous ammonia (25% NH_3) was then added and the slurry transferred to a stainless steel liner. The liner was placed in a stainless steel pressure vessel without a stirring device. The temperature was slowly raised to 300°C and kept at this level for 16 hours at an operating pressure of 1200 psi. The pressure vessel was cooled to room temperature. The product was separated by centrifuging and washing with deionized water and dried at 120°C for 16 hours. The dried material was ground to -48 mesh and calcined in air at 540°C for 6 hours. The calcined material NiSMM was stored in air-tight bottles for further use.

Preparation of NiSMM-Supported Molybdenum Catalyst

NiSMM (50 g) was slurried in 100 mL of deionized water and stirred for 2 hours. A solution of ammonium molybdate tetrahydrate (1.84 g) in 50 mL of deionized water was added slowly to the clay slurry with stirring. After the addition of molybdate, the slurry was stirred for 30 minutes. Excess solvent was removed by evaporation under vacuum. The dried product was calcined in air at 350°C for 3 hours.

Preparation of Fe-Impregnated Center Lignite

As-received Center lignite (250 g, -100 mesh) was slurried in 150 mL of deionized water. A solution of 126.3 g iron(III) nitrate nonahydrate in 100 mL of water was added to the coal slowly with stirring. After the addition of iron nitrate, the stirring was continued for 30 minutes. Excess solvent was removed by evaporation under vacuum.

Final drying was accomplished by heating the coal in a vacuum at 50°C. The resulting coal contained 10 wt% of iron.

Preparation of Iron Hydroxyoxide-Impregnated Center Lignite

Iron hydroxyoxide was supported on Center lignite according to the following procedure: As-received Center lignite (200 g, -100 mesh) was slurried in 400 mL of deionized water and stirred for 2 hours. A solution of iron(III) nitrate nonahydrate (101 g) in 200 mL of deionized water was added to the slurry dropwise with vigorous stirring. After the addition of the iron nitrate, the slurry was stirred for 30 minutes. A solution of 100 g of ammonium hydroxide (28% NH_3) in 200 mL of deionized water was added to the slurry dropwise with vigorous stirring. After the addition of ammonium hydroxide, the slurry was stirred for 30 minutes. The product coal was separated by centrifuging, washed with deionized water, and dried in a vacuum at 50°C overnight. The theoretical amount of iron in the impregnated coal was 10% by weight.

Preparation of Fe-Ca-Impregnated Center Lignite

As-received Center lignite (178 g) was slurried in 200 mL of deionized water and stirred for 2 hours. A solution of iron(III) nitrate nonahydrate (90 g) and calcium nitrate tetrahydrate (7.4 g) in 150 mL of deionized water was added slowly with vigorous stirring to the coal slurry. After the addition was over, the mixture was stirred for 30 minutes, and the slurry was evaporated to remove water. The product coal was dried at 110°C. Upon drying, a highly exothermic reaction began, followed by evolution of pungent gas and flashes of fire. The coal was quickly removed from the oven. However, the exothermic reaction continued for several hours until all of the coal turned brown.

In a separate experiment, another batch of iron-calcium-impregnated coal was prepared according to the above procedure. The drying of the iron-calcium-impregnated coal was accomplished by heating under vacuum at 50°C. No exothermic reaction was observed. However, thermogravimetric analysis of this product resulted in a highly exothermic reaction followed by an explosion.

Iron-calcium-impregnated coal from above was reslurried in 200 mL of deionized water and stirred for 2 hours. A solution of ammonium hydroxide (28% NH_3) in 200 mL of water was added dropwise with vigorous stirring to the coal slurry. After the addition of ammonium hydroxide was over, the stirring was continued for 30 minutes. The product coal was separated by centrifuging and washed with deionized water until free of ammonium hydroxide. The coal was dried by heating in a vacuum at 50°C. Theoretical amounts of iron and calcium in the impregnated coal were 10% and 1% by weight, respectively.

TGA

A DuPont model 951 module interfaced to a DuPont 2100 thermogravimetric analyzer (TGA) and data processor was used in this study. The instrument, shown in Figure 3.3-1, is operated at ambient pressure with a 100-mg capacity and a maximum heatup rate of 100°C/minute. Measurements can be made at temperatures of up to 1200°C. The sample compartment is a quartz tube through which carrier and selected

Figure 3.3-1. TGA reactor module.

gases flow from the balance housing toward the exit port. The quartz tube used in these experiments has a side arm through which a $\frac{1}{16}$ -in. OD stainless steel tube is inserted to allow steam to be introduced to the sample chamber without its passing through the balance housing. The loaded samples were gasified and weight, time, and temperature data were collected by computer for later analysis.

Approximately 50 grams of coal or coal-catalyst were loaded on the balance pan. The quartz tube was then locked in place and argon flow begun. The sample was heated at $100^{\circ}\text{C}/\text{min}$ to 800°C , and the excess steam flow was introduced. The reaction was allowed to continue until approximately 50% of the carbon had been consumed or for 2 hours, whichever occurred first.

IBG

The integrated bench-scale gasifier (IBG) is a small batch process gasifier, with a charge capacity of nominally 70 g of coal. This unit, shown in Figure 3.3-2, provides data on the effects of bed fluidization, conversion of feedstock, reaction rate response to temperature, pressure, catalyst and feed gas composition and flow rate, and gaseous products, while providing sufficient quantities of conversion products for subsequent analysis. In this study, catalysts were screened for their effect on gasification enhancement. Although the IBG serves a purpose similar to that of TGA, it allows a larger-scale collection of multiple gas samples, as well as of liquid and solid products in sufficient quantities for analysis.

Figure 3.3-2 Integrated bench-scale (IBG) reactor.

Although test conditions as high as 850°C and 100 psig were possible, in order to achieve maximum methane yields, thermodynamics requires lowest practical temperatures. However, rates at temperatures below 800°C were too slow to be feasible for gasification of the Illinois No. 6 coal, so most tests with that coal were carried out at 800°C and nominally 50 psig.

Two IBG tests were carried out with catalysts, each having Illinois No. 6 coal fed in two batches. During the first test, IBG065, NiSMM was the catalyst. When the tests were performed, the reactor temperature was stabilized at nominally 800°C. Approximately 55 g of coal-catalyst was fed and the pressure was brought to 50 psig. The product gas was monitored with Fourier transform infrared spectrometry (FT-IR), and when the CO₂ band dropped to approximately 10% of its maximum intensity, a second batch of coal was added. In the second test, IBG072, 21 g of NiSMM catalyst was fed initially and then hydrotreated for 30 minutes. Approximately 50 g of raw coal feed was then introduced. A second batch of coal was introduced after approximately 2 hours.

Test IBG070 was carried out with K-impregnated coal only at 850°C and 50 psig, and IBG071 was carried out similarly, but at 800°C and 50 psig.

Catalytic gasification tests were also carried out on Center lignite. Since the rate-determining step in coal gasification is the rate of fixed carbon conversion, the coal was charged when the reactor temperature was 400°C to allow devolatilization to occur below the carbon gasification temperature. The temperature was increased as quickly as possible to 650°C and held at that temperature to allow gasification of the devolatilized coal.

Table 3.3-3 summarizes the tests carried out in the IBG showing coal, feed weight, catalyst, gasification temperature, gasification pressure, process gases, duration of reaction, and residue recovery. Runs IBG065 and IBG072 involved two separate coal feeds, designated "A" and "B," for which conditions and products were monitored separately. A separate gasification test, IBG075, was carried out without coal to determine whether residues in the reactor might produce methane in detectable quantities. (No detectable methane was found.)

Results

The reactivities determined from TGA data for catalyzed and uncatalyzed steam gasification of the Illinois No. 6 coal shown in Table 3.3-4 are based on change in the weight of the char sample as carbon is gasified. The reactivity was calculated assuming excess steam and first order-kinetics with respect to carbon.

Illinois No. 6 char-steam reactions without catalyst and with admixed nickel-clay and iron-clay catalysts are shown in Figure 3.3-3. Nickel-clay was chosen for the IBG experiments. Table 3.3-5 shows the coal conversion for the IBG tests. Conversions between 40% and 60% in > 1-hr residence time at temperatures of 800°C or greater and without potassium result in insufficient hydrogen and methane to make this gasification feasible as a fuel source for pipeline or fuel cell feed.

The results of initial IBG tests showed that about one-half of the Illinois No. 6 feed coal remained caked in the reactor, forming lumps that were impervious to the reactant

TABLE 3.3-3

The IBG Test Run List (1993)

Test No.	Coal/Catalyst	Temp., °C	Process	Char, yield
65A	30 g NiSMM mixed w/80 g coal, 55 g	800/50psi	N ₂ + Steam, 1 hr	3.0 g
65B	As above, 54.9 g	800/50psi	N ₂ + Steam, 1 hr	Plugged Reactor
66	K ₂ CO ₃ mixed w/Ill. No. 6, 50 g	800/55psi	N ₂ + Steam, 1.3 hr	Plugged Reactor
70	K ₂ CO ₃ mixed w/Ill. No. 6, 55 g	850/49psi	N ₂ + Steam, 1.5 hr	4.0 g 27 g in Hopper
71	K ₂ CO ₃ mixed w/Ill. No. 6, 55 g	800/49psi	N ₂ + Steam, 1.75 hr	10.1 g 10.4 g in Hopper
72	20.85 g NiSMM mixed w/Ill. No. 6 (K ₂ CO ₃), 55.7 g	800/47psi	70% N ₂ + 30% H ₂ , 0.5 hr; N ₂ + Steam, 1.5 hr	No Data
72B	K ₂ CO ₃ mixed w/Ill. No. 6, 55.2 g	800/50psi	N ₂ + Steam, 1 hr	25.8 g
97	Center Lignite, 39.4 g	500-650	N ₂ Only, 1 hr	15.5 g
98	No catalyst, 44.3 g	500-650/ 100psi	N ₂ , 600°C, 30% H ₂ + 70% N ₂ , 1 hr	5.6 g
99	Coal + Fe ³⁺ , 73.1 g	600-650/ 100psi	N ₂ , 400°C, 30% H ₂ + 70% N ₂ , 1.3 hr	33.6 g
100	Coal + FeOOH, 57.1 g	400-650	N ₂ , 640°C, 30% H ₂ + 70% N ₂ , 1.5 hr	23.3 g
101	Fe-Ca catalyst on Center Lignite, 59.4 g	400-650	N ₂ , 400°C, 30% H ₂ + 70% N ₂ , 1 hr	12.78 g
102	Char from IBG101, 12.15 g; Coal Fe-Ca, 42.3 g		N ₂ , 400°C, 30% H ₂ + 70% N ₂ , 2.5 hr	11.4 g
103	Center Lignite + Fe + Ca, 35.77 g		N ₂ , 400°C, 30% H ₂ + 70% N ₂ , 2 hr	7.71 g

gas and, therefore, resulted in a slow reaction rate. In IBG070 and IBG071, the reaction was catalyzed with K⁺ (4) to eliminate the coal's caking tendency. The resulting increase in reactivity at 850°C and 800°C would be offset by a decrease in methane at the higher temperature. In addition, the cost of potassium catalyst is known to be excessive without catalyst recycle, and recycle has not been shown to be successful, probably because of chemical reduction of potassium followed by potassium loss through vaporization.

Gas bags were filled at irregular time intervals over the duration of each test and the contents analyzed by gas chromatography (GC). The mole % of the three gas components of interest, H₂, CO, and CH₄, in the product gas, corrected for carrier gas, are shown in Tables 3.3-6 to 3.3-8.

Nickel had a positive effect on the rate of gasification of bituminous coal. However, the agglomerating property of the coal seriously reduces steam-coal contact surface area even if catalyst-coal contact is maximized, making it difficult to evaluate the catalyst. Addition of potassium to prevent agglomeration of the coal also contributes to the

TABLE 3.3-4

First-Order Reactivities for Catalyzed and Uncatalyzed Illinois No. 6
Steam Gasification

Catalyst	Reactivity, hr ⁻¹		
	800°C	750°C	700°C
None	0.25		
10% Fe-Clay	0.41		
10% NiSMM (Batch 1) 951B	0.41		
10% NiSMM (Batch 2) 1008S	0.41		
K ₂ CO ₃	9.49		
10% NiAc (dry)	0.51		
10% NiAc (H ₂ O)	0.70	0.37	0.17
10% NiAc (H ₂ O/H ₂ S)	0.75	0.30	0.15
10% NiAc (H ₂ O/vac.)	1.16	0.39	0.22

Figure 3.3-3. Metal-clay catalyzed Illinois No. 6 char-steam reaction at 800°C. First-order rate constants are shown.

TABLE 3.3-5

Coal Conversion for IBG Tests

Test	Feed, g	Recovery, g	Conversion, wt%
IBG065	100	52	48
IBG066	111	62	44
IBG070	55	31	49
IBG071	55	25	56
IBG072	139	69	51

TABLE 3.3-6

Percentage of Hydrogen in Product Gas

Time, min	Test Number					
	IBG065	IBG066	IBG070	IBG071	IBG072B	IBG072C
2	30	1	51	60	60	41
4	32			55		
6	42			52		
8		42				
10	44			46	56	
20		43	44			
30			38		23	
40		40	39		29	
50						49
70		37	26			
80		7				43
90		7				
101	35			38		
103	37					
108	49		13			48
130	32					
160	13					

TABLE 3.3-7

Percentage of Carbon Monoxide in Product Gas						
Time, min	Test Number					
	IBG065	IBG066	IBG070	IBG071	IBG072B	IBG072C
2	16	6	21	17	24	46
4	16			28		
6	14			27		
8		17		35		
10				32	34	
20	17	34	41			
30			25		52	
40		41	39		36	
50						30
70		14	33			
80		7				39
90		11				
101		12				
103	14					
108	12		30			20
130	13					
162	11					

TABLE 3.3-8

Percentage of Methane in Product Gas						
Time, min	Test Number					
	IBG065	IBG066	IBG070	IBG071	IBG072B	IBG072C
2	31	8	14	13	14	11
4	34			ND		
6	30			ND		
8		22				
10	28			ND	ND	
20		17	ND			
30			ND		ND	
40			ND		ND	
50						ND
70		27	ND			
80		7				ND
90		12				
101	31	ND		ND		
103	27					
108	27		ND			ND
130	ND					ND
162	ND	ND	ND	ND	ND	ND

ND = not detected.

catalysis of the gasification reaction as seen from Table 3.3-2, making it difficult to assess the respective effects of the individual additives.

As suggested by Figure 3.3-4, methane production appears to be principally a result of pyrolysis rather than a chemical reaction between hydrogen and carbon monoxide. Spectral data from other tests suggested a similar conclusion.

Table 3.3-9 shows the effect of temperature on reactivity for two of the nickel catalyzed reactions. Each increase of 50° C results in a 3-fold increase in reactivity. The increase is of the order expected for temperature effect.

The effect of catalysis on the Center lignite char-steam reaction with various forms of nickel and iron is indicated by the reactivities shown in Table 3.3-9. Catalysis with nickel or iron individually, as with the bituminous coal, had little effect on the reaction rate. However, TGA results showed that the rate of the char-steam reaction, when catalyzed by a combination of impregnated iron and calcium, increased 1.5 times because of the well known rate-enhancing effect of alkaline-earth metals. Impregnated nickel also appeared to increase reactivity over that of the dry-mixed catalyst. Molybdenum in combination with nickel did not increase the reactivity of the coal over that of nickel alone. The catalyzed char-steam reactivity of the lignite coal was 15 to 35 times greater than that of the bituminous under the similar test conditions. The alkali-catalyzed bituminous char-steam reaction had a much higher reactivity, approaching that of the similarly catalyzed lignite char-steam reaction.

Figure 3.3-4. Gas production from Ni-clay catalyzed Illinois No. 6-steam reaction in the IBG at 800°C and nominally 50 psig.

TABLE 3.3-9

First-Order Reactivities for Catalyzed and Uncatalyzed Center Lignite Steam Gasification as Determined from TGA Data

Application	Catalyst	Reactivity, hr ⁻¹			
		650°C	700°C	750°C	800°C
---	None			6.60	
Impregnation	NiAc ₂			7.18	
Dry-Mixed	NiSMM	0.58	2.24	6.37	17.34
Dry-Mixed	MoNiS	0.68	2.22	6.10	17.25
Impregnation	Fe(III)			6.85	
Impregnation	FeOOH			6.56	
Impregnation	Fe-Ca			9.62	

Iron and calcium impregnation onto the lignite from nitrate solutions of the cations resulted in a highly reactive mixture. Rapid oxidation of the coal occurred at room temperature to the extent that the coal was consumed overnight. Removing the nitrate by treatment with ammonium hydroxide resulted in a highly reactive gasification substrate that could be stored overnight without significant loss of coal. Alternative salts of iron and calcium will be selected for preparation of coal-catalyst mixtures in the future to prevent the spontaneous loss of coal and to reduce materials and preparation costs.

Since the pressure is a critical variable in CH₄ production, the effects of the variable pressures observed in three of the tests were normalized to better observe the effects of the catalysts tested. Simple plots of CH₄ absorbance (at various scale factors) are plotted against pressure for Tests IBG098, IBG099, and IBG100 in Figure 3.3-5. Theoretically, the gasification reactions are first-order exponentials, starting with a sharp peak and decreasing at a decelerating rate. A simple linear regression was done on these three data sets, with all absorbances at their original same-scale factors, and for the last two-thirds of the points, where the last two-thirds correspond approximately to the period of gasification, excluding pyrolysis. While the linear correlations still exhibit the effects of randomness with time, it is significant that the data are clustered in three well-defined layers.

While the objectives of this study deal with the effects of the candidate catalysts on hydrogasification, comparison of the FT-IR data for the three runs has indicated an increase in methane production by pyrolysis. In the absence of hydrogen in the feed gas during warm-up, it is a reasonable hypothesis that the presence of the catalyst enhances hydrogasification by the hydrogen produced during pyrolysis as well. Applying the same normalization procedure as used for pressure above, Figure 3.3-6 shows a plot of CH₄ absorbance, on as-received CL coal, to the same original scale factor plotted against temperature for IBG097, IBG098, IBG099, and IBG100. Note the great increase in methane production at temperatures above about 440°C. These curves are probably caused by a composite of rather fast releases of methane by cracking of a wide array of solid and tar structures, occurring at different temperatures. The sudden drop-off above 600°C is because of depletion of the source compounds.

As a preliminary step to scaling up the gasification catalyst testing, hydrogasification tests were carried out in the pressurized TGA. The results showed that, even with catalyst, the reaction rate of hydrogasification of Center lignite under pressure was much slower than that of the char-steam rate obtained at ambient pressure, as seen by comparing the reactivities of 750°C NiSMM-catalyzed reactions in Tables 3.3-9 and 3.3-10. Furthermore, the reactivity of the uncatalyzed hydrogasification of the lignite appeared to be independent of pressure, whereas reactivity with nickel catalysis increased with pressure, as shown in Table 3.3-10.

Methane production during catalyzed gasification was monitored during IBG testing by collecting product gas in bags and analyzing the contents by GC. The methane concentrations in mole % of several bags collected periodically during the tests are shown in Table 3.3-11. The gasification test catalyzed by the combination of iron and calcium not only gave increased reactivity, but also resulted in the highest sustained methane production. The reactivities, along with measured methane production shown in Table 3.3-11, suggest the mechanism for catalyzed pressurized gas-phase reaction shown by equation (1) in which Δm represents the change in number of moles in the gas phase, whereas the results suggest the slower gas-solid phase reaction shown by equation (2) for the pressurized hydrogasification of coal.

An approximation of the gas concentrations from the FT-IR spectrum is possible by applying spectroscopy theory. The concentration of a component of the gas is directly proportional to the absorbance of a specified wavelength. The Beer-Lambert law is an expression of this relationship, given as $A = abc$, where "A" is absorbance, "a" is the molar absorptivity of the species; "b" is the cell path length, and "c" is the specie concentration. The law is quite accurate over reasonable concentration ranges. Applying the law to this series of tests required FT-IR spectroscopic data and known gas concentrations. Gas bag samples were analyzed by GC to determine CH_4 concentration periodically during the test and the absorbance was determined with FT-IR spectroscopy. Molar absorptivities calculated from FT-IR at times corresponding to time of collection of bagged gas samples resulted in a range from 1.8 to 2.8. The range was the result of spikes or dips being occasionally coincident with the GC point. The average molar absorptivity, a, was determined to be about 2.2 and was used to get an estimate of methane concentration during gasification.

Conclusions

It is clearly advantageous to maintain increased pressure to promote methane formation, even, and perhaps especially, at the low flow rates of this series of tests.

Both nickel and iron catalysts were successful, raising methane production significantly but the iron seemed to be more effective during both pyrolysis and hydrogasification phases of the gasification. On-line tracking of the gases with FT-IR spectrometry provides a highly satisfactory monitoring tool for the progress of the process during gasification.

Figure 3.3-5 Methane absorbance, plotted against pressure, during hydrogasification of Center lignite in tests IBG098, IBG099, and IBG100.

Figure 3.3-6 Methane absorbance, plotted against temperature, during hydrogasification of Center lignite in tests IBG097, IBG098, IBG099, and IBG100.

TABLE 3.3-10

Hydrogasification Reactivities for Raw and Catalyzed Center Lignite Char-Steam
Reaction at 750°C at Three Pressures as Determined from PTGA Data

Pressure, psi	Reactivity, hr ⁻¹	
	Raw	NiSMM
150	0.14	0.11
300	0.20	0.16
425	0.20	0.42

TABLE 3.3-11

Methane Concentration in Normalized Mole % Obtained During
Catalyzed and Uncatalyzed Reactions of Center Lignite in the IBG

Time, min	IBG098	IBG099	IBG100	IBG101	IBG102	IBG103
0						
4	0	4	12	0	0	0
12						
14		7			10	
16						2
20	8					
28				0		
34				16		
36						
40				50		
42						
44	21					
46						
48				30		
54		9			0	
60			34			
68				31		
70		21				
72					0	
78					0	21
82			30			
84		36				
86						
88				7		
94	12					
96						
98					10	
102						23
120						31
122						
124			2			
138		21			11	
150						38

Low reaction rates for bituminous coal, even when catalyzed with the best catalysts known to date, preclude their consideration as feedstock for an integrated gasification-molten carbonate fuel cell. Iron-calcium catalyst increased methane production and also increased the rate of the lignite char-steam reaction over that of the Fe-catalyzed gasification. The Fe catalysts show great promise for promoting a gasification product gas stream suitable for fuel cell feed.

Center lignite has a 15 to 35 times higher catalyzed char-steam gasification rate than Illinois No. 6 bituminous coal at ambient pressure. Although Illinois No. 6 produces methane during pyrolysis, gasification is too slow to sustain the initial level of methane production without expensive catalysts such as potassium. The lignite also produced methane during pyrolysis and, with the aid of catalysts, was able to sustain a greatly enhanced methane production during hydrogasification.

Recommendations

- Examine the effect of inexpensive catalysts such as zeolite or dolomite on catalytic tar cracking external to the primary reactor.
- Examine the effect of inexpensive catalysts for tar cracking as a function of temperature.
- Analyze the product to determine selectivity of catalyst.
- Determine whether the catalyst can be recycled.

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TASK 3.0 ADVANCED POWER SYSTEMS

Subtask 3.4 Hot-Gas Cleaning

INTRODUCTION

Many prototype high-efficiency coal-fired power systems require stringent removal of particulate ash from the high-pressure/high-temperature gas stream to prevent erosion of turbine blades or plugging of fuel cells. At present, ceramic candle filters and cross-flow filters have shown the capability to reduce particle loadings in coal-fired gas streams to acceptable levels. However, long-term thermal and chemical degradation of the filters has prevented their reliable use at the relatively high temperatures required. One of the principal degradation mechanisms is attack by alkali vapor and other gases, such as steam, on aluminosilicate binder materials or on the silicon in silicon carbide or silicon nitride materials. The alkali interaction usually leads to the formation of new phases that have different specific volumes or thermal expansion coefficients. The differences lead to spalling of surficial reaction layers, permitting further attack of the underlying material. In addition, alkali vapor and other combustion gases can increase the rate of reaction between the ash particles and the filter, causing the ash to stick to the filter. If the ash cake remains porous it serves as an additional filter layer, but if further interaction with the gas causes the pores to close, the filter will be blinded. The propensity for blinding to occur is a function of filter, ash, and gas properties. Little is understood about the relative importance of these parameters, because an inadequate database of the interactions is available.

OBJECTIVES

The overall objective of the Hot-Gas Cleaning (HGCU) task was to develop reliable methods of removing particulate matter from high-temperature/high-pressure gas streams produced from coal combustion. The primary area of research involved determinations of rates and mechanisms of alkali, steam, and ash corrosion and blinding of ceramic filters. The research focused on reactions occurring at approximately 900°C. Although this temperature is slightly higher than generally used in hot gas systems, it was chosen so as to more severely test the candidate filters and to simulate high-temperature excursions of the HGCU system.

The corrosion and blinding research is being pursued on several fronts, including literature surveys, experimental work, and computer modeling. The experimental work is being performed primarily in the laboratory. Initially, the plan entailed testing large numbers of candidate filter materials in a muffle furnace in the presence of alkali vapor and ash to determine rates and mechanisms of corrosion and strength loss. However, after extensive discussions with industry and METC personnel, it was decided that the rings of filter material would be coated with ash and simulated flue gas containing enhanced alkali vapor levels would be passed through the rings for several hundred hours. At the end of the tests the rings would be notched and the strength of the c-rings would be determined at high temperature under compression. To do this would require the development of experimental methods and the construction of a larger furnace system than was available. In addition to the corrosion and blinding measurements, laboratory

methods were developed for depositing thin coatings of tantalum oxide on silicon carbide (SiC) with the aim of reducing the corrosion rate of SiC candle filters by alkali vapor. Finally, the database for an existing thermochemical equilibrium computer model was greatly expanded, and the model was used to calculate the effect of alkali getter additives on the concentration of vapor-phase sodium species. Finally, an extensive literature search was performed and a plan developed for future expansion of the equilibrium code to include an extensive database and algorithm library together termed a materials knowledgebase. The knowledgebase will be used to calculate the behavior of materials for which no experimental data is available. This knowledgebase will solve the largest single problem in the development of more reliable computer codes that can be used to predict materials behavior. That problem is the lack of data for new materials being used in complex arenas such as coal-fired energy systems.

Bench-scale corrosion research will be performed with bench-scale combustion and gasification systems. The objectives of this work are to determine particulate and vapor phase alkali degradation of candidate ceramic filter structures and/or fixed beds of selected alkali sorbents. Finally, pilot-scale tests will be performed to measure the alkali corrosion of ceramic materials as well as to evaluate filter performance with a hot-gas cleanup test loop attached to the EERC transport reactor development unit (TRDU).

ACCOMPLISHMENTS

Literature Survey of Ash and Alkali Corrosion of Hot-Gas Cleanup Filter Materials

Background

High-temperature chemical corrosion and thermal stresses are known to cause degradation of ceramic particulate filters in direct, coal-fired turbine systems. Severe chemical corrosion occurs in the presence of gaseous alkali, ash, and steam. Also, corrosion is possible from SO₂, H₂S, and other low-level gas contaminants.

At the present time, hot-gas cleanup filters operate at temperatures up to 900°C. SiC candles are formed by bonding ceramic fibers made from SiC and/or grains of alumina-silica bound together by an aluminosilicate-based binder. Ceramic cross-flow filters made from either cordierite or a mixture of mullite, cordierite, and alumina are constructed from multiple layers of thin porous plates that contain ribs to form gas flow channels. Fabric filters are flexible filters made from ceramic fibers (silica-alumina-boria, SiC, quartz, ZrO₂, zirconia-silica, and alumina) formed into a mat or woven cloth and fabricated into bag filters (1, 2).

Candle filters must be cleaned approximately 2-20 times each hour throughout their lifespans (3). The thermal stresses created by blowing cool, pressurized air through the filters to clean them are significant. Cracks are especially formed near the flange region from which the filter is supported (4). Degradation mechanisms include both short-term (<1000 hours) stress effects and long-term (>1000 hours) corrosion effects.

The purpose of the survey was to determine the relative corrosion resistance of commercially available barrier filter materials and to determine the mechanisms of

corrosion so that new filter materials (principally binders) and filter coatings could be developed to increase the corrosion resistance of the filter materials. SiC-based filters were the focus, and three types of corrosion were considered: corrosion by vapor-phase alkali as represented by sodium compounds, corrosion by steam, and corrosion by ash. Three major characteristics of binders are taken into account:

- Corrosion resistance.
- High adhesion of binder with SiC that results in the formation of extended interdiffusion zones.
- Reasonable ratio of plastic/elastic components in the binder to reduce both tensile stresses resulted from cooling and creep during exposure of the filter to high temperature.

Two major properties of protective coatings were considered:

- Corrosion resistance and
- Generation of stresses at substrate-coating interface due to thermal expansion mismatch

Summary of Literature Survey

The silicon carbide filters with clay binders have been most frequently used in-field for coal-fired turbine applications. SiC has been recognized to have an excellent oxidation resistance in air, strength retention to high temperatures, high wear resistance, high thermal conductivity, and good thermal shock resistance. The thermal expansion coefficient is $\alpha = 5.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ in the temperature range 25° – 1500°C . However, the axial thermal expansion coefficient of SiC is affected by the presence of several crystalline polytypes (5). Because of the high percentage of covalent bonding, SiC is difficult to sinter to high densities without binders and/or external pressure.

Silicon nitride can also be used in filter construction. It has excellent high-temperature strength and creep resistance, lower oxidation resistance than SiC, good thermal shock resistance, and good dimensional stability over a wide temperature range. The thermal expansion coefficient for α and β polymorphs are 2.9 and $2.3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, respectively, in the temperature range 25° – 800°C .

Mullite and cordierites are mostly applied as binders to join SiC and/or Si_3N_4 powders. They have low resistivity to high-temperature alkali attack. Thermal expansion coefficients for mullite and cordierite are 5.62 (25° – 1500°C) and $(2.4 - 5.5) \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ (25° – 1000°C), respectively.

Mullite is a candidate for use at high temperature because mullite matrix materials exhibit low thermal expansion, low thermal conductivity and excellent creep resistance (6, 7). Mullite has the general formula $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10x}$ ($0.2 < x < 0.5$), with the most frequently occurring compositions at about $x = 0.25$ ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and $x = 0.40$ ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$). The mullite structure is able to incorporate considerable amounts of transition metal ions, primarily Ti^{3+} , Ti^{4+} , V^{3+} , V^{4+} , Cr^{3+} , Mn^{3+} , and Fe^{3+} ions. Trivalent

chromium ions may substitute for Al^{3+} at up to 12-wt% Cr_2O_3 and also may occur in interstitial sites in the structural channels of mullite. Structural channels are formed by six-membered rings of tetrahedra occupied by Al and Si atoms.

Crystalline mullite is known for very good creep resistance. The diffusional creep rate of polycrystalline mullite (grain size $\approx 3\text{--}4\text{ }\mu\text{m}$) is $\sim 6 \times 10^{-8}/\text{s}$ at 1400°C and 90 MPa and is associated with grain-boundary sliding (8). Mullite with some glassy phase in the grain boundaries shows plastic deformation up to about 11% strain at 1400°C . The diffusional flow of mullite may be facilitated by the addition of ZrO_2 (9). For some zirconia-to-mullite ratios, the composite may exhibit superplastic deformation. Low plastic deformation of the binder is desirable to obtain good thermal-shock resistance.

Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) and cordierite-based glass/ceramics are used as structural materials due to their low thermal expansion and the resulting thermal-shock resistance, low density, and low thermal conductivity (10). The fracture strength of cordierite may be enhanced as pressure is increased from 110 to 260 MPa by dispersing ZrO_2 particles as a second phase. Also, the thermal-shock resistance increases in the $350^\circ\text{--}500^\circ\text{C}$ temperature range by dispersing 15 wt% of ZrO_2 in the cordierite matrix. However, the thermal expansion coefficient increases gradually with increasing ZrO_2 content. For 15 wt% of ZrO_2 , that increase is 0.2%.

Alkali ions such as Na, K, and even Cs can be incorporated into structural channels, causing framework deformation (11).

Alkali Corrosion of Silicate Binders

Sodium appears to begin to react with the clay and mullite binders at about 825°C (12). At higher temperatures, a reaction zone forms on the surface which extends into the binder. It contains high-expanding alkali phases that quickly cause thermal spalling. The absorption capacity of sodium can be increased by a factor of 2.8 in the presence of water vapor at 850°C and a pressure of 11 bars (13). Additionally, the water slowly reacts with silica in the binder and causes its depletion (4).

Generally, loss of binder is caused by:

- Liquefaction resulting from the decrease of viscosity (12)
- Erosion/spalling

Corrosion of SiC

The resistance of SiC to high-temperature oxidation results from the formation of a continuous, adherent surface coating of SiO_2 (14, 15). Vitreous silica is protective in clean oxidizing environments. However, above $1100^\circ\text{--}1200^\circ\text{C}$, this silica coating can become less protective if it begins to crystallize and form a cristobalite phase. This crystallization causes the generation of high tensile stresses during temperature cycling, and thereafter an extensive spalling of the cristobalite layer occurs. Alkali corrosion of silicon carbide is caused by the destruction of this protective SiO_2 surface layer. The concept of acid-base chemistry has been introduced to describe the corrosion of SiC (16). An acidic solution is defined as one with low free-oxide-ion activity; a basic solution is, conversely, one with

relatively high free-oxide-ion activity. Thus the corrosion rate is attributed to the oxygen ion diffusivity, expressed by the following reactions:

A basic oxide (e.g., Na_2O) readily transfers its oxygen to the coordination sphere of an acid oxide (SiO_2) to stabilize a silicon anion (17). The presence of basic salt solutions coupled with an oxidizing agent such as O_2 and H_2O will result in catastrophic attack of SiC. The normally stable, protective SiO_2 layer becomes unstable in these solutions. Some authors proposed the reason water vapor accelerates the oxidation of SiC is that water vapor promotes the crystallization of amorphous silica scale into cristobalite, creating grain boundaries. The major rate-determining step for SiC corrosion is the inward diffusion of water and outward diffusion of CH_4 through the silica scale. Steam can also dissolve silica from refractories.

Alkali and steam have also recently been shown to greatly increase the rate of interaction between an ash cake and the silicon carbide in the filter (18). Normally, ash interactions with silicon carbide at HGCU temperatures is very limited. However, in the presence of alkali and steam the reaction is much more rapid, and the major reaction products are calcium and magnesium silicates for western coal ash, and sodium aluminosilicates for eastern coal ash (18) since sodium silicate is not thermodynamically stable in the presence of other ash constituents (see the description of the thermochemical equilibrium modeling of alkali gettering later in this report).

The protective SiO_2 layer is very resistant to attack by SO_2 - SO_3 - O_2 gas mixtures below 1000°C (19). No evidence of sulfate formation exists, and no thermodynamic data is available for silicon sulfate. However, deposits of salts such as Na_2SO_4 tend to enhance the gaseous corrosion below 1000°C . The activity of Na_2O in the sulfate is inversely proportional to the SO_3 pressure. The extensive degradation of the protective layer of vitreous silica by sodium is caused by the devitrification of silica.

The corrosion of vitreous silica under reducing conditions (low-oxygen atmosphere) with an excess of H_2S may occur by the formation of SiS vapor (20). A major problem for refractories in petrochemical applications is the removal of silica by hydrogen-rich gases. Stringer (21) has reviewed the problem associated with refractory and ceramic construction materials in petrochemical and coal-gasification environments.

Resistance of various aluminosilicates to alkali attack was found to be enhanced by increasing the alumina content up to 60%. Sodium may react with alumina, forming sodium aluminates at temperatures above 1100°C (22).

Summarizing, high-temperature alkali corrosion research has focused primarily on the following structural ceramics: silicon carbide (23-30), silicon nitride (25, 26, 30), cordierite silicon nitride (31), mullite, alumina, aluminum titanate, zirconia and fiberglass (32).

Reduction in Mechanical Strength of Candle Filters

Mechanical degradation of candle filters is caused by the differential pressure across the filter, vibrations, thermal gradients, installation and handling, the weight of the candle, and accumulated dust (4). The major source of mechanical degradation is believed to be caused by thermal shock from pulse cleaning resulting from the generation of thermal stresses at the SiC-binder interface because of the mismatch of linear thermal expansion coefficients. Thermal stresses may increase if alkali chemically reacts with the binders. Table 3.4-1 shows the effect of sodium content on the variation of linear thermal expansion coefficients for selected aluminosilicate glasses (33). These changes are expected to occur in binders when sodium is absorbed. Some of the silicates are

TABLE 3.4-1

Thermal Expansion Coefficients and Viscosities for Selected
Silicate Glasses Taken from the *Handbook of Glass Properties* (33)

Composition, mol%			$\alpha \times 10^{-6}/^{\circ}\text{C}$	$\log \eta$,	Temperature,
Na ₂ O	B ₂ O ₃	SiO ₂	20°–300°C	Poise	°C
2	28	70	3.6	10	634
4	21	75	3.2	10	765
6	24	70	4.1	10	716
8	22	70	4.7	10	711
10	20	70	5.6	10	648
Na ₂ O	ZrO ₂	SiO ₂	20°–400°C		
10	10	80	4.9		
10	20	70	4.9	12.5	548
15	5	80	7.0		
25	5	70	10.5		
30	5	65	12.0		
MgO	Al ₂ O ₃	SiO ₂	25°–600°C		
20.3	18.3	61.4	4.31		
25	15	60	3.7	10	1500
35	15	50	4.5		
Na ₂ O	Al ₂ O ₃	SiO ₂	20°–100°C		
17	15	68	7.6	10	670–780
20	37	43	7.7		
25.3	28.0	46.7	10.5		

already used as binders. The viscosity of selected silicates seems to be high, about 10^{10} poise, but not high enough to avoid plastic deformation. The creep is known to occur around the softening point of glass. The softening point of glass is the temperature at which the viscosity is approximately $10^{7.6}$ poise. At this viscosity, a rod about 24-cm long and 0.7 mm in diameter elongates 1 mm/min under its own weight. Under constant pressure the plastic deformation will occur at higher viscosities.

Thermal stresses in the SiC-binder system can lead to decohesion when critical values are exceeded, which manifests itself in stable growth of interfacial cracks and separation along the SiC-binder interface. Separation at the interface occurs when loading direction is depended on: either the tensile stresses perpendicular to the interface exceed a critical value (δ_i), or the interfacial shear stresses exceed a critical value (τ_i). Tensile normal stresses can arise during cooling when the thermal expansion coefficient of the binder is higher than that of the SiC or as a consequence of tensile deformation of the SiC-binder system by external forces. Local tensile stresses at the interface, detected by the existing defects and/or formed as a result of inhomogeneities, stimulate the nucleation of cavities, leading to predamage that lowers the adhesive strength. Compressive stresses can arise if a thermal expansion coefficient of the binder is lower than that of the SiC and external forces.

Generally, tensile stresses in the binder (such as might be caused by its larger thermal expansion coefficient) are relevant to the propagation of cracks in a brittle substrate (34). Also, the compressive stresses in the binder parallel to the interface may lead to tensile stresses perpendicular to the interface at the SiC, causing a lift of binder from the SiC and binder separation. The latter effect is mostly detected during corrosion of metals (35).

The above analysis of stresses at the binder-SiC interface is used to predict trends in the breakdown of the binder cohesion. The effects of binder thickness, elastic properties, and SiC toughness are not taken into consideration.

Table 3.4-2 lists two additional potential binders that may be employed in SiC-based barrier filters (36).

The Role of Additives and Coatings in Corrosion Protection of SiC-Clay Materials

As mentioned earlier, the densification of SiC is extremely difficult to accomplish. However, additives such as boron, carbon, and a wide variety of rare earth oxides, usually in combination with Al_2O_3 , promote densification at temperatures around 2000°C (37). The major problems with these additives result from the formation of volatile components such as CO and SiO during oxidation of the SiC. In the use of silicon carbide in harsh environments, the SiC must develop a vitreous coating to prevent rapid oxidation. The inward diffusion of corrosive gases through the vitreous coatings is lower than that along the grain boundaries in most crystalline coatings. To improve the corrosion resistance of SiC in highly corrosive, industrial stack-gas environments, plasma-sprayed ceramic coatings have been applied, including single-layered mullite and multilayered coatings of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$), alumina, yttria, chromia, mullite- Al_2O_3 , mullite- Y_2O_3 , and yttria-stabilized zirconia (38, 39). The coatings were more adherent to SiC bounded by binders than to the sintered SiC. Criteria for well-adherent, corrosion-

TABLE 3.4-2

Physical Properties of Binder Materials for SiC

Material	Melting Temperature, °C	Thermal Expansion Coefficient, (x 10 ⁻⁶), °C ⁻¹	Temperature Range, °C
SiC (reference)	2500	5.1	25-1000
Zirconia Mullite	1743	6.5	20-1130
ZrSiO ₄	1760 (T _d)	4.2	25-700

resistant coatings for SiC up to about 1300°C are: to be similar to the SiC coefficient of thermal expansion, to have a low modulus of elasticity, and to be a precursor available to a commercial plasma-spray powder (40). Recently, a two-layer system incorporating a plasma-sprayed, Y₂O₃-stabilized zirconia over an underlying plasma-sprayed NiCoCrAlY bond coat has been investigated for turbine engines. Also, indium (In₂O₃) was selected as a candidate resistant to high-temperature reactions with SO₃, Na₂SO₄, and vanadate melts. Results of these tests are not yet available.

Some coatings, such as alumina, are excellent protection in the absence of sulfur compounds. Severe degradation of Al₂O₃ may occur because of the reaction with molten Na₂SO₄ film which may proceed by acidic or basic fluxing reactions (19):

Researchers at the Virginia Polytechnic Institute, Center for Advanced Ceramic Materials, have reported a new high-temperature barrier material based on the composition (Ca_{1-x}, Mg_x)Zr₄(PO₄)₆ (CMZP) (41). The CMZP materials have near-zero bulk thermal expansion and low crystal anisotropy, adjustability from positive to negative thermal expansion coefficients by controlling composition and processing parameters, very low thermal conductivity, thermal stability at 1500°C, excellent thermal-shock resistance, and good resistance to alkali attack (41). These materials are postulated for use as coatings to protect silicon-based ceramics for alkali corrosion. Information is not yet available about the adhesion of CMZP materials to silicon-based ceramics.

In addition, researchers at Oak Ridge National Laboratory have found that tantalum pentoxide can be deposited on SiC by chemical vapor deposition (42). The coatings bond well, and their coefficients of thermal expansion match that of the SiC well enough to preclude spalling. The coatings are extremely resistant to alkali salt attack at 1000°C. However, research at the EERC (reported in a subsequent section of this report) has shown that similar electron-beam-deposited coatings are not resistant to attack by silicate ashes at 1300°C.

SiC and Metallic Binders

In the past five years, SiC-metal composites have been increasingly studied. Most research was conducted with pure Ni, Fe, Ni-Fe alloys, Ti, Cr, and with Ni-Cr and Ni-Cr-Al alloys (43, 44). These metals react with carbon and silicon by forming a broad class of reaction products such as carbides and silicides, respectively (45). The mechanical, thermal, and chemical stability of the systems during service critically depends on the integrity of the interface between the metallic and ceramic components. The adhesion in such systems increases with increasing affinity of the metal for carbon. A limited number of ceramic-metal bonds exist that are stable at high temperatures. Two major restrictions, the high thermomechanical stresses and the thick reaction layers, limit the utilization of metals as binders for structural ceramics. Reaction layers usually have inferior properties compared with the joined materials, thereby reducing the stability and strength of the joint. More recent work has focused on other promising binding alloys, such as MoSi_2 , that may improve high-temperature mechanical properties and oxidation resistance of composites (46). A disadvantage to this alloy is poor thermal-shock resistance during rapid heating.

Experimental Work With Ta_2O_5 Corrosion-Resistant Coatings for SiC

Ta_2O_5 Corrosion Resistant Coatings for SiC

Background

As described in the previous section, high-temperature corrosion of ceramic structural materials in hot-gas cleanup systems, heat exchangers, and other ceramic components used in coal combustion systems has lead to an ever increasing need for new materials and technology. Much of the research in this area has focused on the mechanisms involved in the corrosion of advanced high-temperature ceramics such as SiC. In efforts to prevent the corrosion work has been done to find coatings for SiC materials to protect them from corroding from the products of coal combustion and gasification. In this section, we report on progress made in the development of tantalum pentoxide as a corrosion-resistant coating for SiC. In addition, we describe the possible use of this technology in joining applications.

At high temperatures, SiC forms a protective oxidation layer of SiO_2 (47). In the presence of alkali vapor this layer reacts to form alkali silicate glasses such as sodium silicate. This sodium can then react with the silicon carbide causing corrosion (48-50). Thus to prevent corrosion, the coating must be able to resist reaction with alkali vapor, as well as with ash particles. Also, because the coating will undergo thermal cycling from room temperature to as high as perhaps 1400°C , it must have a thermal expansion coefficient similar to that of SiC to prevent spalling.

Of all the coating materials that have previously been tested, the two which seem to hold the most promise are mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and tantalum pentoxide (Ta_2O_5). Although mullite has a coefficient of thermal expansion of $5.7 \times 10^{-6}/^\circ\text{C}$, very close to that of SiC ($5.5 \times 10^{-6}/^\circ\text{C}$), its corrosion resistance is dependent upon the formation of stoichiometric mullite. Free SiO_2 in non-stoichiometric mullite would corrode and dissolve the native SiC- SiO_2 oxide layer. Since forming stoichiometric mullite may prove to be difficult, Ta_2O_5 was chosen as the first coating to study. Phase equilibrium diagrams of

the $\text{Ta}_2\text{O}_5\text{-Na}_2\text{O}$ (51) and $\text{Ta}_2\text{O}_5\text{-SiO}_2$ (52) systems indicate no liquid phases of sodium tantalate exists below 1625°C and no tantalum silicates are present below 1550°C (53). Also, Ta_2O_5 has a low coefficient of thermal expansion of $3.6 \times 10^{-6}/^\circ\text{C}$.

Tantalum and tantalum pentoxide have long been used in thin film microelectronic devices (54–59). Several methods exist for deposition of dense, uniform Ta_2O_5 films including chemical vapor deposition (CVD) (60–62), physical vapor deposition (PVD) (63–66), and anodic oxidation (67–87) and thermal oxidation (88) of tantalum films. Research at Oak Ridge National Laboratory is currently being done to develop a technique for chemical vapor deposition. This work has lead to some degree of success; however some of the crystalline films that were produced have a columnar grain structure which could provide a path for corrosion or reaction of sodium with the SiC. Work there has now turned to optimizing the coating morphology to produce smaller more equiaxed crystal grains (60). Research at the EERC has been undertaken to develop techniques for producing coatings using physical vapor deposition, namely electron beam deposition of Ta_2O_5 , and a combination of electron beam deposition of tantalum metal and subsequent anodic oxidation to Ta_2O_5 .

Electron-Beam Deposition

In electron-beam deposition, a high-power beam of electrons is accelerated at high voltage and focused onto a pool of material to be deposited. The process is carried out inside a vacuum chamber. The kinetic energy of the electrons is converted to thermal energy upon striking the material to be deposited. This material is thus vaporized by the electron beam and is deposited on anything in the chamber within its line of sight.

The electron-beam evaporator is capable of vaporizing any known substance. Compounds may be stoichiometrically evaporated and deposited providing they do not decompose or disassociate, unless the dissociated species are made to recombine either in the vapor state or, more likely, at the surface of the substrate to be coated. Reactive evaporation (89) is also possible in which two or more materials are evaporated simultaneously and then reacted with each other. A purge gas can be introduced into the vacuum through a leak valve to maintain the required partial pressure for reaction. In this way many metal nitrides, oxides, carbides, silicides and other compounds including Ta_2O_5 are routinely evaporated to produce high-quality optical coatings, protective coatings, and microelectronic devices in industry (90–102).

Large electron-beam evaporation systems are commercially available that can coat aluminum onto anything from plastic cellophane to structures as large as aircraft engine turbine blades. Leybold AG designed and built a system capable of deposition rates from 0.001 to 1000 nm/sec (66). The deposition rate is easily controlled by simply varying the power to the electron beam. Because this technique has such a wide range of applicability and is commercially available, it should prove to be a good candidate for applying anticorrosion coatings to SiC and other materials used in hot-gas cleanup systems.

Experimental

The electron-beam evaporator used in producing the coatings was donated by Vacuum Technology Corporation of Minneapolis MN. It was manufactured by CHA industries and has a power supply capable of producing a 6-kilowatt or 10-kV electron

beam at a current of 600 milliamperes. It has a high-vacuum, oil diffusion pump that produces an ultimate vacuum of 10^{-8} torr in the evaporation chamber. An array of 5 1200-watt, quartz infrared heaters in the chamber provides 6000 watts of power to heat the substrates up to 450°C . A needle valve was installed on the system to allow introduction of gases for reactive evaporation. The system is equipped with an Inficon XTC quartz-crystal thickness monitor, which measures evaporation rate and film thickness. Sample-mounting fixtures supplied with the instrument are motor driven and provide a means of planetary rotation of the samples around the evaporant for more uniform coatings.

The tantalum used to produce Ta_2O_5 and Ta coatings was donated by Tosoh SMD, Inc. and was of 99.9% purity. To make the Ta_2O_5 , the tantalum was cut into small pieces and oxidized in air at 1000°C . The tantalum emerged in a powder form and was placed into the water-cooled copper crucible which serves as the hearth for the evaporant in the electron gun. Two-inch-diameter Hexaloy SA SiC washers donated by Carborundum company were cut into four pieces to provide substrates for coating. The washer sections were prepared for coating by first cleaning with methanol and then preoxidizing at 1350°C for 12 hours. The purpose of the preoxidation was to grow a thick, initial oxide layer and to stabilize the surface for the coating. The samples were then mounted to the planetary fixture in the electron-beam evaporation chamber along with one microscope slide. Because of the ease in which glass microscope slides can be broken and a limited supply of SiC, slides were used in all SiC coating runs as sacrificial samples for testing and analysis.

The system was then pumped down to a pressure of 2×10^{-6} torr, at which time liquid nitrogen was added to the cold trap, and the substrate heaters were turned on to outgas the chamber. The chamber was heated to 400°C for 20 minutes for outgassing, then the substrate heaters were set to maintain a substrate temperature of 250°C , measured by a K-type thermocouple located near the sample holders. An oxygen supply, attached to the vacuum system through a needle valve, was then set to bleed in oxygen until a pressure of 2×10^{-4} torr was reached. Maintaining an oxygen partial pressure is a standard technique used to recombine dissociated tantalum at the surface of the substrate. A shutter was then placed over the hearth, and the electron beam was turned on. The beam current was increased slowly to outgas the oxide and achieve a homogenous melt. After a steady state had been achieved, the shutter was opened and evaporation commenced.

Three washer sections were coated using deposition rates of approximately 10, 15, and $75 \text{ \AA}/\text{sec}$, using electron-beam currents of 150, 250, and 250 milliamperes respectively. Rotating on the planetary fixture, the samples maintain an average distance of 40 cm from the source. To achieve the highest rate of $75 \text{ \AA}/\text{sec}$, the sample was mounted in a stationary position 20 cm from the source, instead of on the planetary fixture. The result was approximately a fourfold increase in deposition rate, as would be expected from an inverse-square relationship of evaporant flux density with distance. After coating, the samples were cooled to room temperature under vacuum and removed for examination. A visual inspection showed the films to be very dense and uniform. The coatings varied in color from transparent for the $10\text{-}\text{\AA}/\text{sec}$ coating to translucent brown for the $15\text{-}\text{\AA}/\text{sec}$ and an almost opaque black for the $75\text{-}\text{\AA}/\text{sec}$ coating. The variation in color was likely due to higher nonstoichiometric quantities produced by increasing the deposition rate. At low evaporation rates, the oxide was either not dissociated significantly or oxygen in the chamber combined with the freshly deposited substoichiometric oxide to form a clear

stoichiometric oxide coating. At high-evaporation rates, the tantalum oxide partially decomposed, and oxygen may not have had time to recombine with dissociated tantalum oxide at the surface of the substrate.

Figure 3.4-1 is a secondary electron image of a 27-micron coating evaporated onto a glass slide and broken to produce the cross section shown. This opaque black film was deposited using the 75-Å/sec deposition rate. No grain structure is visible, indicating a relatively amorphous coating, although x-ray diffraction would need to be used to confirm this. Line scans using energy-dispersive x-ray (EDX) spectroscopy were done across the cross section to determine variations in the tantalum and oxygen content in the coating. Figure 3.4-2 shows a line scan of the coating initiating near the surface and proceeding toward the substrate. As can be seen, the oxygen content gradually decreased toward the surface of the coating. This trend was due to the depletion of oxygen in the tantalum pentoxide evaporation source in the hearth under bombardment of the electron beam.

A slag corrosion test was then performed on the coated SiC samples. The samples were placed in an alumina crucible filled with glass powder prepared from Illinois No. 6 coal ash. To prepare the glass, the ash was melted at 1650°C and homogenized at this temperature for 4 hours. The glass was then quenched on a brass plate to room temperature and ground into a fine powder. The samples were covered with the glass powder in the alumina crucible and placed into the furnace for slagging. The glass was heated slowly into a melt at 1300°C, and the temperature was held for 48 hours. The samples were then allowed to cool slowly and removed for sectioning and SEM analysis.

Figure 3.4-1. Secondary electron image of 27-micron tantalum oxide coating on a glass microscope slide.

Figure 3.4-2. EDX line scan of coating.

Results and Discussion

Upon sectioning the samples, large voids were observed in the slag, which were apparently produced from gas bubbles forming in the slag. These bubbles are presumed to be CO or CO₂ formed during oxidation of the SiC after dissolution of the initial SiO₂ layers. The samples, therefore, had very poor coverage by the slag. SEM analysis showed little coating by either the slag or the tantalum pentoxide films and, as a result, showed little or no corrosion. The tantalum oxide coatings appeared to have been partially dissolved and then broken up by the gas bubbles. A small area of slag adhesion, which contained tantalum grains, was observed in one experiment in which the sample was tested at 1260°C for 132 hours. Figure 3.4-3 shows the area where a large concentration of tantalum grains were present within the slag. This area appeared to be a wall separating two adjacent gas bubbles that emanated from the sample. The black areas on either side of the slag are the void areas from the bubbles. It is reasonable to assume the gas bubbles broke up the film, after which the tantalum oxide grains became concentrated in these areas. Figure 3.4-4 is a higher-magnification view of the tantalum oxide grains. Table 3.4-3 shows the composition of the tantalum oxide grains and the composition of the adjacent slag. The grains were composed mainly of tantalum, iron and silicate phases. The slag adjacent to them appeared to have dissolved some amount of tantalum oxide. The slag around the grains was likely saturated with tantalum oxide, which would prevent complete dissolution of the grains as seen here.

The coating along the slag-SiC interface appears to be still intact in this small area. What may be a corrosion pit appears directly beneath the coating with what seems a gas

Figure 3.4-3. SEM backscattered electron image of the SiC-slag interface showing the remains of the tantalum pentoxide film.

TABLE 3.4-3

Composition of the Material Shown in Figure 3.4-3

Oxides	Illinois No. 6 Ash, wt%	Slag, wt%	Tantalum Grains, wt%
Na ₂ O	1.18	1.18	0.19
MgO	2.50	0.71	0.33
Al ₂ O ₃	18.50	16.15	1.82
SiO ₂	57.80	61.38	9.22
K ₂ O	0.62	2.50	0.00
CaO	3.74	4.08	0.28
TiO ₂	1.03	0.29	2.10
FeO	14.62	5.68	16.23
NiO	ND*	0.89	0.00
Ta ₂ O ₅	ND	7.02	69.65

*Not determined

bubble emanating from it. This bubble was probably from CO or CO₂ formed from oxidation of the SiC. Gas formation at the SiC-coating interface would be detrimental to any kind of coating and may be the cause of the separation of the films.

Conclusions on Corrosion Resistance of Electron-Beam Deposited Tantalum Oxide Coatings

After the conclusion of these slag corrosion experiments, two key papers were found on recent work in the systems Na₂O-B₂O₃-Ta₂O₅ (103) and Al₂O₃-B₂O₃-Na₂O-Ta₂O₅ (104). According to this work Ta₂O₅ has up to 40-wt% solubility in a sodium borosilicate-alumina matrix when melted at temperatures between 1350°C and 1400°C. This same behavior might also be expected in the aluminosilicates from which slag is composed. Therefore, it has been shown that this coating will probably not be of any protective use for SiC in the event of direct slag contact at 1350°C or at ash slagging temperatures. Further work may continue on the capability of tantalum pentoxide to protect SiC from corrosion in hot gas conditions with no slag contact, or perhaps at temperatures below which the ash begins to fuse. The technique of electron-beam deposition, however, is useful for applying coatings of a very wide range of materials that may be useful as coatings to protect refractory materials such as SiC from corrosion.

Anodic Oxidation of Electron-Beam Deposited Tantalum Metal

In addition to directly depositing tantalum oxide on a SiC substrate, depositing tantalum metal on the substrate and then oxidizing the tantalum in situ was tried to see if the anodized grain structure provided better corrosion resistance. In anodic oxidation, the material to be oxidized becomes the anode of an electrolytic cell. The anode reacts with negative ions from an electrolytic solution and becomes oxidized, forming a protective oxide coating. The details of the ion-transport process are still a subject of some debate (67, 68). If the anode material conducts electricity, a metal oxide film may be formed from the anode material itself. Alternatively, depending on the nature of corrosion resistance needed, the anode may be coated with a suitable metal, which is then oxidized in the anodization process, forming the protective coating desired.

The thickness and rate of growth of an anodic film depends on the current density, temperature, and the composition of the electrolyte. For the case of constant current, growth increases linearly with time, and the cell voltage must be continuously increased to counter the increased resistance as the film thickens. At constant cell voltage, the film grows rapidly—on the order of minutes—approaching a limiting practical value where additional time produces an impractical increase in thickness. The drop in growth rate is rapid enough to enable reproducible thicknesses for a given voltage. A number of metals exhibit anodic oxidation. Some of those, which most readily form a dense film, are listed in Table 3.4-4 along with some electrolytes and the corresponding maximum practical oxide thickness developed per volt.

The upper limit in film thickness is determined by the breakdown potential, which occurs at about 1,100 volts for Al (resulting in a 1.5-micron-thick film) and 700 volts for Ta (giving a 1.1-micron-thick film) (67). Interest in anodization of tantalum dates back to the early 1950s from work on making capacitors in the electronics industry (69). In most cases anodic oxide films are amorphous, and the anodization of tantalum is no exception

Figure 3.4-4. SEM secondary electron image of the tantalum pentoxide grains at higher magnification.

TABLE 3.4-4

Anodization Parameters for Metals that Form Dense Oxide Films

Material	Oxide	Electrolyte (20°C)*	Oxide Thickness, Å/Volt
Aluminum	Al_2O_3	Ammonium citrate	13-14
Antimony	$\text{Sb}_2\text{O}_{3\text{and}4}$		
Bismuth	Bi_2O_3		
Hafnium	HfO_2		
Niobium	Nb_2O_5	Ammonium tartrate	16
Tantalum	Ta_2O_5	1 part by weight of oxalic acid + 2 parts water + 3 parts ethylene glycol at 105°C	25
		Ammonium borate	16
Titanium	TiO_2	Ammonium tartrate	22
Tungsten	WO_3		
Silicon	SiO_2	0.4 mole KNO_3 in N- methylacetamide	4.6
Zirconium	ZrO_2		

*Unless otherwise stated

(86, 87). The anodic film that forms on tantalum results from the combination of tantalum with oxygen ions in the reaction

Since oxygen is present in water in the form of hydroxyl ion, the half cell reaction is generally written as:

This equation represents the formation of 10 equivalents or 1 mole of oxide, since there are 10 electrons per molecule that must be transferred. A mole of tantalum oxide weighs 442 grams, and 10 faradays (965,000 ampere-seconds) of electricity must be passed through the cell in this reaction.

Experimental

The experimental arrangement used in this laboratory to produce anodic tantalum films consists of a beaker or electrolytic cell with a cathode of tantalum or platinum, as shown in Figure 3.4-5.

A 300-volt DC power supply was used in series with a current-limiting ballast resistor, an ammeter, and the electrolytic cell. Because there was no access to a constant current supply, only the constant voltage technique was used. For initial testing, the

Figure 3.4-5. Schematic of experimental arrangement of anodic cell.

anode was prepared by electron-beam evaporation of a thin film of pure tantalum onto a microscope slide and anodizing to a potential of 200 volts. The electrolyte used consisted of 1 part by weight of oxalic acid, 2 parts water, and 3 parts ethylene glycol heated to 105°C, similar to that used by previous researchers (69).

Upon anodization, the growing film exhibited interference colors of many orders of magnitude indicating that the tantalum was indeed being anodized and that it was on the order of several thousand angstroms in thickness. Using this electrolyte, a thickness limit of 25 Å/volt should be achieved (Table 3.4-4), producing an anodic film of 5000 Å at 200 volts. After this initial test, coupons of silicon carbide were also coated with a thin film of tantalum metal and anodized under identical conditions to the microscope slide.

Results and Discussion

In the course of experiments on anodizing the tantalum-coated SiC, it was found that the SiC coupons conduct electricity well enough to effectively short out the cell, causing anodization to stop. This halt in anodization occurred because of coating of the SiC on only one side by the electron-beam evaporator. As the anodic film on the coated side of the SiC grew, its resistance increased above that of the bare silicon carbide. Thus the current took the more favorable path through the uncoated side, and the anodization stopped.

Conclusion

As a result of cell shortage, no successful anodic tantalum pentoxide films were produced to date on SiC. Future work to produce these coatings will require the SiC substrate to be completely covered by a uniform tantalum metal coating, preventing contact between SiC and the electrolyte to prevent shortage. A small fixture was developed that permits the SiC sample to be rotated in the chamber of the evaporator. This fixture allows the SiC to be coated with tantalum on both sides so that only the tantalum is exposed when placed in the electrolyte, and complete anodization occurs.

Construction of a Reactor for Measuring Corrosion and Blinding of Filter Materials

A hot-gas reaction furnace was constructed, and initial shakedown testing was performed. A schematic drawing of the reactor is shown in Figure 3.4-6. The reactor allows the introduction of a very wide variety of gas mixtures to simulate corrosive atmospheres and combustion conditions at pressures up to 2 psig. It consists of a mullite retort 6 inches in diameter and 6 feet long with 48 inches of it heated. The mullite retort has stainless steel end caps that are sealed to the retort with high-temperature silicon-based adhesive. The end caps have ports for introducing and exhausting gases, introducing water vapor, measuring pressure, and measuring exit gas temperature and relative humidity. The retort pressure, exhaust gas temperature and relative humidity data are acquired by computer for overnight monitoring of changes in the system during the course of experiments.

Gas mixtures are controlled by an array of four precision rotameters allowing five gases, including water vapor, to be mixed in the desired proportions. The water-vapor content is governed by the evaporation rate of water in the steam generator attached to a

port on the end cap. Experiments were performed to calibrate the steam generator for a number of evaporation rates to produce water-vapor contents in the range of combustion environments.

As can be seen in Figure 3.4-6, the furnace has three independently controlled temperature zones, one 24-inch center zone, and two 12-inch end zones. The total 48-inch heated length provides a uniformly heated length of approximately 30 inches. The furnace has a maximum operating temperature of 1100°C. The center-zone controller has a 16-segment ramp and soak feature to allow for unattended thermal cycling or annealing of the samples. The outer two zone controllers are single-set-point controllers with 2-segment control, one ramp and one soak with an end process of either hold or off.

Experimental

Testing in the hot-gas reactor is currently underway to determine the hot-gas corrosion resistance of a candle filter produced by Third Millennium Technologies Inc. A gas composed of 66.5% nitrogen, 15% carbon dioxide, 15% water vapor, 3% oxygen, 0.5% sulfur dioxide, and 10 ppm sodium sulfate vapor is to be passed through a filter coated with a thin layer of fly ash at a rate of 10 liters/min. The filter will be tested under this gas composition for up to 500 hours at 900°C. After corrosion testing, the filter will be cut into "c" rings one-inch wide for strength testing with a method known as the c-ring test. The c-ring tests will be performed at 900°C in the same atmosphere using an Instron 8562 universal testing machine fitted with a high-temperature muffle furnace.

Figure 3.4-6. Schematic of the hot-gas reactor.

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3 of 4

Thermochemical Equilibrium Modeling

Background

The chemistry of coal combustion is an extremely complex process. Based on the conventional characterization of coal as a sulfo-nitryl hydrocarbon matrix embedded with fairly significant concentrations of inorganic or ash constituents (such as Al, Si, Fe, Na, K, Mg, Ca, Ti, and P compounds), a conservative estimate of the number of just the dominant inorganic combustion products yields about 400 chemicals. The inclusion of elements such as Hg, Pb, Cr, As, Cd, Se, and Ni present in trace-level concentrations—the so-called trace elements—increases the total to around 550 chemicals or about 1650 species. Any reasonably complete model of the coal combustion process must thus not only address the reaction mechanisms for the formation and interaction of these 1600-odd species (each of which could easily burgeon into hundreds of reaction steps), but must also deal with the transport and flow characteristics of the reactants and products, the effects of oxidizer/reducer flow rates, the nonlinear interactions between combustor geometry and reactant flow (which results in flow, temperature, and pressure inhomogeneities), heat-transfer mechanisms, and other operational parameters such as thermal shedding and sootblowing frequency. Significant progress has been made in many of these areas (105–107). Nevertheless, the intrinsic complexity of the problem, coupled with the magnitude of computations involved, precludes the application of the current states of the art to provide quick solutions to some of the more immediate concerns of the coal combustion industry, such as air toxic emissions control.

On the other hand, the modeling and characterization of combustion processes in general and that of vapor-phase trace metal species in particular, purely in terms of equilibrium thermochemistry, is a relatively uncomplicated and straightforward process. Equilibrium thermochemistry can provide information regarding the dominant reaction mechanisms and thus the equilibrium manifold or attractor set of the system. It can also provide good estimates on the upper bounds of the concentrations of the system phases and their constituent species. Since the equilibrium description is concerned only with the long-term or asymptotic behavior of the system, the dynamical description of the system's evolution to equilibrium is, of course, lost. But in many cases, an understanding of the system's equilibrium is needed to understand its dynamics; in other cases, the equilibrium behavior is all that is needed (as in systems with short-lived transients or very short relaxation times). Thus equilibrium thermochemistry is a basic and useful tool for analyzing and modeling diverse thermodynamic phenomena. Indeed, application areas include analysis of plume structure in multiphase submerged combustors (108), design of a water-purification process where it is necessary to describe vapor-liquid equilibria for aqueous solutions containing weak electrolytes (109), determination of the properties of explosives (110), liquid-metal, fuel-propulsion systems (111), coal gasification (112, 113), phase diagram calculations (114–117), characterization, remediation and management of gas streams and fly ash in coal combustion processes (118–122), coal liquefaction (123), crustal geochemical processes such as seawater metasomatism of basalt, diagenesis of an arkose, etc., (124–126), equilibrium geochemistry of the planets (127), and others.

In this section, the primary focus is on the description of the equilibrium distribution of the vapor-phase trace elements in coal combustion and related processes. The chemical equilibrium problem is formulated and analyzed in detail in the following section. In the subsequent section, the TEACH software package is described. TEACH,

port on the end cap. Experiments were performed to calibrate the steam generator for a number of evaporation rates to produce water-vapor contents in the range of combustion environments.

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Figure 3.4-6. Schematic of the hot-gas reactor.

an acronym for Thermodynamic Equilibrium Analysis of Coals and asHes, is a computer program being developed as part of a long-term study of the equilibrium thermochemistry of coal and coal combustion. The current status and accomplishments of the thermochemical equilibrium modeling subtask is summarized later in the report (Conclusions and Future Work). A detailed description of how TEACH will be incorporated into the overall trace element evolution model and what tasks need to be undertaken to accomplish this rounds off this section.

Thermochemical Equilibria

The problem of obtaining the equilibrium composition of complex chemical mixtures is a classic problem that has been and still continues to be extensively addressed (128–148). Numerous software packages such as NASA-CEC (145), PACKAGE (118), SOLGAS (133, 134), SOLGASMIX (135), MPEC2 (139), etc., have been reported in the literature and their relative merits discussed as well (140, 148). While most of these codes are found to perform adequately, a few instances of misleading or erroneous results also seem to appear (137, 138, 140). In addition, many of these packages require a priori estimates of the phases present at equilibrium, which introduce additional uncertainties in the computed results, especially when the Gibbs free energy of the system is nonconvex (136–138, 140, 148). Indeed, depending on the initial estimate, convergence to a local minimum is often achieved, and thus special tests need to be performed to ensure the globality of the computed minimum. Reference 138, for instance, provides "phase-splitting" algorithms for this purpose.

In the so-called ideal model (140, 147, 148), the Gibbs free energy of the system is, in general, not differentiable along the boundary of the feasible set. In addition to this geometric obstruction, nondifferentiability of the free energy may also arise when the system undergoes a phase transition, and some of the system's macroscopic parameters become discontinuous or unbounded. Although this physical obstruction is not all too important in view of the manner in which the minimization problem is usually formulated, it nevertheless serves to emphasize the importance of a rigorous determination of the equilibrium phases. Therefore, any algorithm designed for minimizing the Gibbs free energy must require its differentiability, if needed, only in the (relative) interior of the feasible set. To overcome this limitation and to utilize the elegant Lagrange multiplier formalism, many of the programs cited earlier handle the boundary points by various ad hoc methods that, in general, are not guaranteed to converge. It may be noted that Lagrange multiplier formulations of optimization problems for nondifferentiable functions do exist; however, in these formulations, the concept of a derivative is either generalized (e.g., subdifferential), or a completely different methodology is adopted (149, 150). The TEACH algorithm requires the differentiability of the free energy only within the interior of the feasible set and thus avoids the inherent instabilities induced by abrupt changes or other pathologies.

Another potential problem exists in the case of multiphase systems, especially with regard to the ideal model. This problem is the possible nonuniqueness of the optimal point realizing the minimum of the free energy of the system; in fact, the set of points minimizing a convex function is itself convex and thus a continuum of "indifferent" equilibrium states may arise (140–143). (This situation usually occurs along phase boundaries.) An elegant and physically compelling solution to this problem in terms of the "generalized lever rule" is given in (142), also incorporated into TEACH. (A thorough

explanation of indifferent equilibria states in terms of center-manifold and integral-manifold theory is given in [151] where the notion of dormant instabilities is introduced and an analysis of the dynamics of coexisting phases is also given.)

A precise statement of the chemical equilibrium problem can be formulated as follows: let $\mathcal{C}$ be a closed thermodynamic system at a specified temperature T and pressure P . (As a general guide for notations and terminology, reference 140 is adopted.) The system $\mathcal{C}$ contains N chemical species $\mathcal{C}_1, \mathcal{C}_2, \dots, \mathcal{C}_N$ constituted from M elements $\epsilon_1, \epsilon_2, \dots, \epsilon_M$. The element abundance vector $\mathbf{b} = (b_1, \dots, b_M)^t$ (superscript t denotes "transpose") specifies the number of moles of each element ϵ_i so that, since the system $\mathcal{C}$ is closed, the mass balance equations

$$\mathbf{A}\mathbf{n} = \mathbf{b} \quad [\text{Eq. 1}]$$

must be satisfied by the species abundance vector $\mathbf{n} = (n_1, n_2, \dots, n_N)^t$, where $\mathbf{A}$ is the formula matrix whose a^{th} row and j^{th} column matrix element A_{aj} represents the number of moles of element ϵ_a in one mole of species $\mathcal{C}_j$. Additionally, the components of the species abundance vector $\mathbf{n}$ must be nonnegative,

$$n_j \geq 0, j = 1, \dots, N \quad [\text{Eq. 2}]$$

The system $\mathcal{C}$ is partitioned into Γ subsets $P^1, P^2, \dots, P^\Gamma$ called "phases" whose union covers $\mathcal{C}$

$$\bigcup_{\alpha=1}^{\Gamma} P^\alpha \supseteq \mathcal{C} \quad [\text{Eq. 3}]$$

Associated with each phase P^α is its Gibbs free energy function G^α , which is defined to be a continuous, real-valued function

$$G^\alpha: \mathcal{P}^{N_\alpha} \rightarrow \mathbb{R}: \mathbf{n}^\alpha \mapsto G^\alpha(\mathbf{n}^\alpha) \quad [\text{Eq. 4}]$$

where N_α is the number of species in phase P^α , $\mathbf{n}^\alpha = (n_1^\alpha, \dots, n_{N_\alpha}^\alpha)$ is the species abundance vector of phase P^α and $\mathcal{P}^{N_\alpha}$ is the non-negative hyperoctant of $\mathbb{R}^{N_\alpha}$,

$$\mathcal{P}^{N_\alpha} = \{\mathbf{x} \in \mathbb{R}^{N_\alpha}: x_i \geq 0\} \quad [\text{Eq. 5}]$$

The overall Gibbs free energy (G) of the entire system is given by¹

¹ Assuming that the phases are noninteracting or that interphase interactions are negligible.

$$G = \sum_{\alpha=1}^r G^{\alpha} \quad [\text{Eq. 6}]$$

The chemical equilibrium problem can now be expressed as the minimization program,

$$\inf \{G(\mathbf{n}) : \mathbf{n} \in \Omega\} \quad [\text{Eq. 7}]$$

where Ω is the feasible set

$$\Omega = \{\mathbf{n} \in \mathcal{O}^N : \sum_{\alpha=1}^r \sum_{j=1}^{N_s} A_{aj}^{\alpha} n_j^{\alpha} = b_a\} \quad [\text{Eq. 8}]$$

Two questions arise, viz., existence and uniqueness. Before addressing these, we first analyze the feasible set. From the definition of the formula matrix $\mathbf{A}$, namely, that the a^{th} row and j^{th} column element A_{aj} equals the number of moles of element ϵ_a in species $\mathcal{C}_j$ it is clear that

- (i) $\mathbf{A}$ is a nonnegative matrix, i.e., $A_{aj} \geq 0, \forall a, j$
- (ii) $\forall j, \exists a$ such that $A_{aj} > 0$.

"(ii)" is merely an expression of the fact that each species $\mathcal{C}_j$ is built from one of the M elements $\epsilon_1, \dots, \epsilon_M$ and hence, that at least one of its stoichiometric coefficients must be positive.

Another simple result can be obtained from the formula matrix by making the (almost always true) assumption that the number of elements, M , is not greater than the number of species, N , i.e.,

$$M \leq N \quad [\text{Eq. 9}]$$

In this event, the rank $r(\mathbf{A})$ of the formula matrix $\mathbf{A}$ is not greater than the number of elements, M ,

$$r(\mathbf{A}) \leq M \leq N \quad [\text{Eq. 10}]$$

From now on we shall only consider systems for which Eq. 10 is always true.

Lemma 1: Let $\mathbf{A}$ be the formula matrix of the system $\mathcal{C}$, $\mathbf{b}$ an abundance vector for $\mathcal{C}$, and $\mathbf{n}$ a feasible vector in the feasible set Ω given by Eq. 8. Then,

$$a) \quad \bar{A}_{.j} > 0$$

$$b) \quad 0 \leq n_j \leq n_j^u = \min_{1 \leq a \leq M} \left\{ \frac{b_a}{A_{aj}} : A_{aj} > 0 \right\}$$

$$c) \quad \frac{\bar{b}}{\max_{1 \leq j \leq N} \{\bar{A}_{.j}\}} \leq \bar{n} \leq \frac{\bar{b}}{\min_{1 \leq j \leq N} \{\bar{A}_{.j}\}}$$

Lemma 2: The feasible set Ω is a compact convex polytope.

The convexity of Ω follows straightforwardly from the linearity of the defining equations. On the one hand, the previous Lemma shows that Ω is bounded; on the other, since $\mathbf{A}$ can be regarded as a linear (hence continuous) map from $\mathbb{R}^N$ to $\mathbb{R}^M$, it immediately follows that Ω is closed. We merely need to invoke the Heine-Borel theorem (152), to claim the compactness of Ω .

One of the results of convexity theory (153, Theorem 3.16.13) asserts that a compact convex subset is the convex hull of its extreme points. An extreme point of a convex set K is a point of K that cannot be expressed as a convex linear combination of any pair of points of K , neither of which is itself. (In the language of linear programming, an extreme point is a basic feasible solution [154, Theorem 3.1]). Hence,

Corollary 1: The feasible set Ω is the convex hull of its extreme points.

The question that immediately arises is whether the extreme point set is finite or otherwise. Borrowing a result from linear programming again (154, Theorem 3.5.3), we have

Corollary 2: The set $\text{Ext}(\Omega)$ of extreme points of Ω is finite with

$$|\text{Ext}(\Omega)| \leq \binom{N}{r(\mathbf{A})}$$

where $r(\mathbf{A})$ is the rank of $\mathbf{A}$, and for nonnegative integers r and N , $\binom{N}{r}$ is the binomial coefficient

$$\binom{N}{r} = \frac{N!}{(N-r)! r!}$$

The kernel $\ker(\mathbf{A})$ of the formula matrix $\mathbf{A}$ is also of interest. Elements of $\ker(\mathbf{A})$ are reaction vectors representing actual chemical reactions. Thus any matrix $\mathbf{K}$ that is a right divisor of zero of $\mathbf{A}$

$$\mathbf{AK} = 0$$

[Eq. 11]

is termed a reaction matrix.² A reaction matrix whose columns (which are reaction vectors) constitute a basis for the kernel of $\mathbf{A}$ is defined to be a complete reaction matrix. Complete reaction matrices play an important role in the formulation of mass action laws (141), determination of the dominant reactions and reaction products, and in the solution of the chemical equilibrium problem via stoichiometric algorithms (110, 111, 140).

Lemma 3: Let the formula matrix $\mathbf{A}$ be expressible as $\mathbf{A} = \mathbf{I}_M + \mathbf{R}$, where $\mathbf{I}_M$ is the $M \times M$ unit matrix and $\mathbf{R}$ is a $M \times (N - M)$ nonnegative matrix. Then

a) The feasible set Ω is nonempty and $\begin{bmatrix} \mathbf{b} \\ \mathbf{0}_{N-M} \end{bmatrix}$ is in Ω , where $\mathbf{0}_{N-M}$ is the $(N - M)$ -dimensional zero vector.

b) The matrix $\mathbf{K}$ defined by $\mathbf{K} = \begin{bmatrix} -\mathbf{R} \\ \mathbf{I}_{N-M} \end{bmatrix}$ is a complete canonical reaction matrix.

c) Let $\mathbf{D}$ be the $(N - M)$ diagonal matrix

$$\mathbf{D} = \begin{bmatrix} n_{M+1}^u & & \\ & n_{M+2}^u & \\ & & n_N^u \end{bmatrix}$$

and let the $M \times (N - M)$ matrix $\tilde{\mathbf{R}}$ be defined as $\tilde{\mathbf{R}}_j = \mathbf{b} - n_j^u \mathbf{R}_j$, $j = M + 1, \dots, N$.

Then the column vectors of the matrix $\mathbf{V} = \begin{bmatrix} \tilde{\mathbf{R}} \\ \mathbf{D} \end{bmatrix}$ form a linearly independent set of extreme points (vertices) of the feasible set Ω .

d) The matrix $\tilde{\mathbf{K}}$, defined by

$$\tilde{\mathbf{K}} = \begin{bmatrix} [-n_{M+1}^u \mathbf{R}_{M+1}, \dots, n_N^u \mathbf{R}_N] \\ \mathbf{D} \end{bmatrix}$$

is also a complete reaction matrix although it is not canonical.

² We prefer the term "reaction matrix" over "stoichiometry matrix" that is advocated in reference 140.

It may be noted that the above Lemma is extremely useful in understanding the structure of the feasible set. Although the formula matrix $\mathbf{A}$ need not, in general, have the special form required by the Lemma, it can be brought to this form whenever there exists a feasible basis. Thus, the utility of the Lemma is fairly general. The vertex matrix $\mathbf{V}$ shows that Ω contains at least $N - M + 1$ vertices. Lemma 2 provides an upper bound (which, in practice, is very conservative). The reaction matrix $\tilde{\mathbf{K}}$ is, as mentioned earlier, not canonical. However, it has the advantage that reaction extents become completely standardized, varying between 0 and 1, if points of Ω are expressed in terms of $\tilde{\mathbf{K}}$.

We now address the questions of existence and uniqueness of the chemical equilibrium problem as stated in Eqs. 7 and 8. To make the problem meaningful, from here on we will assume that the feasible set Ω is nonempty. For any well-posed problem, Ω is usually nonempty, so assuming a nonempty Ω a priori is not too restrictive. (In any event, at the computational level, the algorithm can be made to terminate if it is determined that Ω is empty.) The continuity of the free energy G and the compactness of Ω then enable us to conclude the following:

Lemma 4: G attains its infimum and supremum on Ω . That is, there exist points $\mathbf{n}_*$ and $\mathbf{n}^*$ in Ω such that

$$G_* = G(\mathbf{n}_*) = \inf \{G(\mathbf{n}): \mathbf{n} \in \Omega\}$$

$$G^* = G(\mathbf{n}^*) = \sup \{G(\mathbf{n}): \mathbf{n} \in \Omega\}$$

Likewise, the convexity of Ω , the continuity of G , and the fact that compact, connected subsets of $\mathbf{R}$ are closed, bounded intervals (155, Theorem 8.4) yield

Corollary 3: The image $G(\Omega)$ of the feasible set Ω is a closed bounded interval of $\mathbf{R}$,

$$G(\Omega) = [G_*, G^*]$$

In general, the Gibbs free energy of the system may exhibit local minima in addition to the global minimum G_* . However, if G is a convex function, then any local minimum is also a global minimum (156, Theorem 6.2.6). This is elaborated in

Corollary 4: Let the Gibbs free energy G of the system $\mathcal{C}$ be convex. Then

- a) Any local minimum of G is also a global minimum.
- b) The set $\Omega_* = \{\mathbf{n}_* \in \Omega: G(\mathbf{n}_*) = G_*\}$ of minimizers of G is a closed, convex subset.
- c) If G is strictly convex, i.e., if for each $\mathbf{n}, \mathbf{m} \in \Omega$ and $\alpha \in (0, 1)$, $G(\alpha\mathbf{n} + (1-\alpha)\mathbf{m}) < \alpha G(\mathbf{n}) + (1-\alpha)G(\mathbf{m})$, then G has at most one minimizer.

It may be observed that part b) of the above corollary is the mathematical statement of the manifold of indifferent or degenerate equilibrium states discussed earlier. Furthermore, in contrast to linear optimization problems, G may well attain its infimum at points interior to the feasible set Ω . Although nonuniqueness appears to be directly related to the convexity of the free energy, the physical reasons for the nonuniqueness must be borne in mind: when a system is undergoing a phase transition, the relative

amounts of the coexisting phases are not fixed. Thus nonuniqueness is a direct consequence of the physics of the situation; convexity of G enforces the physics (157).

A particularly important convex Gibbs free energy is the ideal free energy corresponding to ideal systems. We recall that the Gibbs free energy G^α of a phase P^α can be expressed as (158)

$$\begin{aligned} G^\alpha &= \sum_{j=1}^{N^*} \mu_j^\alpha n_j^\alpha \\ &= \sum_{j=1}^{N^*} n_j^\alpha (\mu_j^\alpha + RT \ln a_j^\alpha) \\ &= \sum_{j=1}^{N^*} n_j^\alpha [\mu_j^\alpha + RT \ln x_j^\alpha(\mathbf{n}) + RT \ln \gamma_j^\alpha(\mathbf{n})] \end{aligned} \quad [\text{Eq. 12}]$$

where

$$\mu_j^\alpha = \text{chemical potential of species } \mathcal{C}_j \text{ in phase } P^\alpha \quad [\text{Eq. 13a}]$$

$$\mu_j^\alpha = \text{standard chemical potential of species } \mathcal{C}_j \text{ in phase } P^\alpha \quad [\text{Eq. 13b}]$$

$$a_j^\alpha = \text{activity of species } \mathcal{C}_j \text{ in phase } P^\alpha \quad [\text{Eq. 13c}]$$

$$\gamma_j^\alpha = \text{activity coefficient of species } \mathcal{C}_j \text{ in phase } P^\alpha \quad [\text{Eq. 13d}]$$

$$R = \text{universal gas constant} \quad [\text{Eq. 13e}]$$

$$x_j^\alpha(\mathbf{n}) = \text{mole fraction of species } \mathcal{C}_j \text{ in phase } P^\alpha \quad [\text{Eq. 13f}]$$

$$= \frac{n_j^\alpha}{n^\alpha} \quad [\text{Eq. 13g}]$$

Depending on the choice of the activities, or the activity coefficients, a variety of approximations to the free energy of the system may be studied. There exist a variety of such approximations such as the Debye-Hückel formulas, Redlich-Kwong, NRTL, Wilson, Wohl, Margules, and Lee-Kestler equations, regular solution and sublattice models, and so on (110, 114, 116, 117, 136–138, 140, 158).

The activities defined by

$$\begin{aligned} a_j^\alpha(\mathbf{n}) &= 1, \text{ if } P^\alpha \text{ is a pure condensed phase} \\ &= P x_j^\alpha(\mathbf{n}), \text{ if } P^\alpha \text{ is a gaseous phase} \\ &= x_j^\alpha(\mathbf{n}), \text{ if } P^\alpha \text{ is a liquid phase} \end{aligned} \quad [\text{Eq. 14}]$$

constitute the ideal model, which has been extensively addressed in the literature (110, 114, 128–136, 140–148), and its relevance to silicate and coal combustion systems has also been emphasized (159, 160).

Lemma 5: Let G_I^α be the ideal free energy of phase P^α . Then

a) G_I^α is defined³ and continuous on the nonnegative hyperoctant $\mathcal{P}^N$.

b) G_I^α is positively homogeneous, i.e.,

$$G_I^\alpha(\lambda \mathbf{n}) = \lambda G_I^\alpha(\mathbf{n}), \forall \lambda > 0$$

c) G_I^α is convex, i.e.,

$$\forall \alpha, \beta \geq 0, \alpha + \beta = 1, \quad G_I^\alpha(\alpha \mathbf{n} + \beta \mathbf{m}) \leq \alpha G_I^\alpha(\mathbf{n}) + \beta G_I^\alpha(\mathbf{m})$$

$$d) \quad \sum_{j=1}^{N^*} \hat{\mu}_j^\alpha n_j^\alpha - \bar{n}^\alpha \ln N^\alpha \leq G_I^\alpha(\mathbf{n}) \leq \sum_{j=1}^{N^*} \hat{\mu}_j^\alpha n_j^\alpha$$

TEACH

TEACH, an acronym for Thermodynamic Equilibrium Analysis of Coals and asHes, is a Gibbs free energy minimization program being developed at the EERC as part of a long-term study of coal combustion and related processes. The development of TEACH was motivated by the need for an effective, robust, and accurate software tool that can be utilized in understanding the equilibrium thermochemistry of coal and coal-ash systems, as well as by the need for a tool that can be applied to other areas of combustion modeling. TEACH is a direct outgrowth of the PHOEBE chemical equilibrium program that was also developed at the EERC but is no longer supported.

TEACH essentially comprises three modules: an input data preprocessor, a minimization engine, and a postprocessor (Figure 3.4-7). The preprocessor facilitates problem specification, data entry, thermodynamic database access/retrieval, data validation and error reporting. In earlier versions of TEACH, the preprocessor was integrated into a TBI (text-based interface) that was operable only on IBM®-compatible PCs. However, since it is envisaged that TEACH will be ported to a number of different systems, the TBI has been dropped, and the user communicates to the program through data files and command line options. In addition to facilitating the porting process, this allows batch jobs to be executed rather easily.

A TEACH input file is a simple ASCII file that contains one or more statements. Statements come in two varieties: data statements and command statements. Data statements are the means by which the user supplies parameter values and units (such as the system's temperature, pressure, excess air and so on), defines the system (by describing the type, state, and constituents of admissible phases and by providing the thermodynamic parameters for the constituent species), defines new compounds (such as,

³ With the convention that $\lim_{t \rightarrow 0} t \ln t = 0$

Figure 3.4-7. TEACH design overview.

for example, a coal compound), functions (say, for instance, functions to compute the net vapor-phase trace metal and alkali concentrations), and macros (primarily to provide symbolic constants). On the other hand, command statements are imperative and require the preprocessor, the minimizer, or the postprocessor to perform specific tasks. Command statements are provided to read from, write to, and embed (or include) files. Commands also exist to perform some system-level functions such as directory searches and invocation of child processes. However, TEACH currently contains no conditional, branch, or iteration statements.

Figure 3.4-8 depicts a typical TEACH input file. As can be seen, the minimal input data statements needed are the temperature, pressure, and amount statements. The title data statement, though optional, should invariably be included since it serves to self-

```

Title = "Effects of Adding Kaolin to Robinson Coal";
Temperature [F] = 1000, 2000,[2200, 2500, 100];
Pressure [psig] = 500;
Amount Robinson [g] = 100,
    Kaolin [% Robinson.ash] = [0, 10, 1],
    Air = AirAmount (Robinson),
    Excess Air [% air] = 30;

```

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Figure 3.4-8. TEACH sample input file.

document the input data file and can also be used as part of the header information in the output files documentor in related report generation. The syntax of the **temperature** and **pressure** statements are self-explanatory except perhaps for the rubric [2200, 2800, 100] in the temperature statement. This is an iteration specification: [2200, 2800, 100] means iterate for temperatures from 2200° to 2800°F in steps of 100°F. The **amount** statement highlights a number of interesting features of TEACH. The word "Robinson", for instance, is part of TEACH's vocabulary and is understood to represent a coal compound of a specific composition. TEACH comes with a database of about 25 U.S. and international coals. (This database can be modified, expanded, etc., by the user at his or her discretion.) The units for the additive kaolin are expressed as a percentage of the amount of ash in the coal. (This is useful when the effectiveness of kaolin in modifying the properties of the ash is analyzed.)

The amount of air fed into the system is expressed in terms of the function "Air Amount" which, by default, computes the stoichiometric air needed to combust the coals supplied as arguments or can be specified by the user. In addition, some excess air, expressed as a percentage of the stoichiometric air, is also specified.

The extraction of the syntactic and semantic content of such an input file is the provenance of a parser that is part of the TEACH preprocessor. The parser reads the input file, converts it into a sequence of lexical classes or tokens and inputs them to a finite state machine (FSM) to both verify the syntactic validity of the sequence of tokens and to perform semantic "actions". In the majority of the cases, these semantic actions simply reduce to the initialization or assignment of system parameters; in other cases, the actions are more involved, ranging from macro expansions and function compilations to abstract syntax tree (AST) generation. The parser, or at least parts of it, also interacts with the minimization and postprocessing modules when these require the evaluation of dynamically defined expressions and functions.

A sophisticated chemical equilibrium problem solver or minimizer forms the heart of the TEACH package. The minimization module can be decomposed into a initialization submodule and a refinement submodule. The initialization submodule is a generalized linear program (GLP) that serves to compute an approximate minimizer to the Gibbs free energy. The refinement submodule then, if needed, iteratively refines this initial

estimate to a more accurate solution. In many instances, especially in the presence of single-component condensed phases at equilibrium, the GLP solution itself converges to a very accurate solution, thus obviating the need for further refinement.

Figure 3.4-9 provides an overview of the GLP algorithm. In broad terms, a GLP can be considered to be a linear program (LP) but with an infinite number of columns in the simplex tableaux (130, 131, 143) since the cost vector of a GLP is really a cost vector function giving rise to an infinitude of cost vectors for each feasible point. More precisely, let $\{G^\alpha: \alpha = 1, \dots, \Gamma\}$ be a finite family of convex subsets of $\mathbf{R} \times \mathbf{R}^M$ and consider the minimization problem

$$\inf \left\{ \sum_{\alpha=1}^{\Gamma} c^\alpha n^\alpha \right\} \quad [\text{Eq. 15a}]$$

subject to the constraints

$$\sum_{\alpha=1}^{\Gamma} n^\alpha p^\alpha = b \quad [\text{Eq. 15b}]$$

$$(c^\alpha, p^\alpha) \in G^\alpha \quad [\text{Eq. 15c}]$$

$$n^\alpha \geq 0 \quad [\text{Eq. 15d}]$$

The peculiarity of GLPs is that the cost vector components c^α and the constraint matrix columns p^α are themselves unknowns of the problem, in addition to the usual solution vector n . Thus a solution to the GLP stated in Eqs. 15a-d is a triplet (n_*, c_*, p_*) where n_* a minimizing vector, c_* the associated cost, and p_* the associated constraint matrix. In general, the GLP need not have any solution at all. A sufficient condition to guarantee existence of solutions is the compactness of the convex sets G^α and the boundedness of the constraint set of Eq. 15b. (The algorithm in Figure 3.4-9 can be used to determine existence of solutions as well.)

The third and final module of TEACH is the postprocessor. In its default mode, it simply writes to the output file the values of the system parameters, and the equilibrium phase and species distributions for each iteration set. In nondefault modes the postprocessor functions primarily like a formatter and can be programmed to structure the output in a variety of styles which can then be imported into other applications for additional processing (such as spreadsheets and graphics packages). Although the

Figure 3.4-9. Initialization GLP algorithm.

postprocessor can be utilized to perform complicated and complex computations to derive other parameters from the equilibrium data, this will impose a significant overhead on the execution time of TEACH. Thus the postprocessor should be used essentially to format the output, and the calculation of additional derived quantities should be undertaken separately.

Conclusions and Future Work

Significant progress has been achieved in the area of thermochemical equilibrium modeling. Major enhancements to the equilibrium analysis program TEACH developed at the EERC include the following:

- A sophisticated GLP minimization engine.
- A versatile input data preprocessor that contains macro expansion utilities and a LALR(1) parser.
- An integrated database access and retrieval subsystem.
- A library of standard and some of the more well-known equation-of-state (EOS) and solution-and-mixture models permitting the analysis of nonideal systems.
- A thermodynamic database of about 5000 species that includes all the phases relevant to coal combustion systems. (The database contains the trace element species as well, although some of the more rare phases are currently absent. Methods of obtaining or estimating the thermodynamic data for these phases are being evaluated.)
- Capability to conduct parametric studies and optimize system performance. (Figure 3.4-10, for example, depicts a 3-D plot of the net equilibrium vapor-phase Hg species as a function of the carbon-to-oxygen ratio and system temperature that was produced using TEACH. Figure 3.4-11 is another 3-D plot of the net equilibrium vapor-phase alkali species as a function of the system temperature and additive (kaolin) amount produced, also using TEACH. Parametric system profiles such as these are extremely valuable in understanding, analyzing, and optimizing system performance; indeed, in addition to providing relations between operational parameters, these also permit simulations of system behavior in nonconventional operational regimes.)
- Capability to format and postprocess the equilibrium data (thereby facilitating interapplication communications and promoting applications reusability).

In the area of future work, the most important issue that needs to be addressed is the incorporation of TEACH into the overall model under development to predict trace element particle-size and composition evolution. As has been discussed so far, TEACH is a stand-alone application in its current version. In view of its complexity and its rather extensive thermodynamic database, it is neither feasible nor advisable to imbed TEACH within another application that is itself expected to be fairly substantial and complex. Since it is desired that the trace element particle-size and composition distribution (PSCD)

Figure 3.4-10. TEACH-predicted net equilibrium vapor-phase Hg.

Figure 3.4-11. TEACH-predicted net equilibrium vapor-phase alkali.

program executes on DOS-based PCs, its size and complexity must be constrained to the limits imposed by the operating system.

The mechanism of pipes for interapplication communication is a standard, and possibly the easiest, way to accomplish the integration. However, a couple of problems exist with this: one is that the PSCD model requires TEACH output within an iteration loop (thus requiring a 2-way pipe, which, at present, is not provided by any operating system). The second problem has to do with system memory constraints, since implementing the interapplication communication via pipes requires that both applications execute concurrently (although, possibly asynchronously).

An elegant solution, with none of the drawbacks discussed above, to integrating TEACH and the PSCD model is provided by artificial neural networks (ANN). Broadly speaking, ANNs represent the connectionist model of the brain in which (external) stimuli are predicated to trigger a bank of input nodes or neurons. The response of the input nodes to the external stimuli are in general nonlinear; these responses are passed via edges (or dendrites) through one or more hidden layers of nodes that also respond nonlinearly. Finally, the net response of the overall network of nodes (or brain) is communicated to the external world through another bank of output nodes. Although ANNs have their conceptual underpinnings in neurophysiology, they are, from an abstract mathematical viewpoint, completely equivalent to statistical (nonlinear) regression, and thus can be used to approximate any continuous function. We refer the reader to the literature (161, 162) for further information regarding ANNs.

The training of the ANN to (implicitly) establish the requisite correlations between equilibrium phase or species concentrations and system parameters is thus the primary task that needs to be completed prior to embedding the network into the PSCD model. Once the training is complete, the ANN can be used by the PSCD model within iteration loops or otherwise but without any penalties in terms of execution time or other system resources. Further, future revisions of TEACH do not impact adversely on the maintenance of the PSCD model, and enhancements to the equilibrium values can be incorporated effortlessly by retraining the network and relinking it to the package.

Further work will thus be directed towards the training of an ANN and embedding it into the PSCD model.

Experimental Measurements and Thermochemical Equilibrium Modeling of Sodium Gettering

Although most of the elements that reach the vapor-phase during combustion condense as ash and sometimes deposit, small portions of the more volatile elements remain in the vapor phase. In particular, sodium and potassium sulfates, chlorides, and hydroxides can reach concentrations of several hundred parts per million by weight at the exit of the combustor. These vapors can cause corrosion of combustor surfaces, hot-gas cleanup systems, or turbine blades. To prevent corrosion, it may be necessary to remove a large portion of the vapor-phase alkali from the gas stream. One method is to use coal additives or beds of materials known as alkali getters to adsorb irreversibly the alkali. Adsorption works through two mechanisms. Materials such as kaolinite, emathlite, and montmorillonite absorb the alkali by chemically incorporating it into their structures.

Other materials like bauxite tend to serve as nucleation sites for condensation of the alkali.

In addition to composition, the degree of interaction between the getter and the combustor gas will affect its efficiency of adsorbing alkali. The most efficient adsorption will occur through extensive interaction between the vapor and the getter. Maximum interaction will occur if the gas stream is very turbulent or if the particles are small and have a high surface area-to-volume ratio. Turbulence in the gas stream is a function of system design, but it can be induced in the vicinity of the getter by keeping the getter in a fixed or fluidized bed through which the gases must pass. However, bed operation is difficult and adds significantly to the capital cost of the system. Particle size is more easily controlled. To prevent excessive getter deposition in the system, particle aerodynamic diameter should be kept below 10 microns. However, to enhance collectability (especially in a wet scrubber system) and minimize the opacity of particulate emissions, aerodynamic diameters should be kept above 1 micron. Finally, the getter should have a composition that is not likely to become sticky once it has adsorbed sodium.

Of all of the gettering candidates reported in the literature (163–166), kaolin clay best meets these requirements. Therefore, its efficiency was tested in both atmospheric and pressurized combustion conditions in the EERC pressurized drop-tube furnace (PDTF) system as reported in the January through June 1992 Semiannual Technical Progress Report of the project entitled "Hot-Gas Cleanup" (167). Kaolin is usually composed of platelets that have diameters of between 1 and 5 microns. As long as it is deagglomerated before or during combustion, the platelets will naturally fall into the perfect size range for gettering. Deagglomerating such particles before combustion is nearly impossible without slurring, so the degree of deagglomeration during combustion was measured in combustion tests. Also, kaolin is composed of approximately $\frac{1}{2}$ alumina and $\frac{1}{2}$ silica, so that after absorption of sodium it will have a much higher solidus temperature than if a pure silicate (like emathlite) is used. Because the easiest method to employ a getter in a utility combustor is to mix it with the coal, that method was used in the combustion tests. However, it is the least efficient method of inducing getter/gas interaction, so the combustion tests that we employed provided a minimum value for gettering efficiency of kaolin.

During this reporting period, TEACH was used to predict the equilibrium concentrations of vapor-phase sodium as functions of gas temperature and getter concentration in a boiler system burning a high-sodium coal. The data was compared to the results of PDTF tests of the gettering efficiency of kaolin. The TEACH package was specifically tailored to the analysis of combustion and combustion-related problems for these comparisons. One such "tailoring"—the ability to conduct parametric studies (i.e., perform simulations) of the thermodynamic behavior of the system—has made TEACH very useful in the understanding of the alkali vapor-sorption mechanisms as well as in the assessment of the efficiencies of various sorber reagents. This modification has made TEACH a design tool that can be used to optimize sorption efficiency in terms of system operating parameters, fuel amounts and compositions, and sorber amounts and compositions. Although many of the reactions occurring in combustion systems are kinetically limited and may not be fully equilibrated, the equilibrium behavior determines the dominant reactions and the maximum extent of the reactions. Thus equilibrium chemistry governs both the alkali vapor production and maximum sorber efficiency.

Results and Discussion

Experimental Work

As reported in the January through June 1992 Semiannual Technical Progress Report of the Hot-Gas Cleaning project (167), tests of the gettering efficiency of kaolin clay were performed with the EERC pressurized drop-tube furnace system. A high-sodium subbituminous coal from the Spring Creek Mine, Montana, was burned in a total of four tests: two at atmospheric pressure and two at 109 psig. For each pressure, one run was made with raw coal and the other with ground kaolin mixed with the coal in a ratio of one part kaolin to two parts ASTM coal ash. The ash was collected after combustion with Cyclones 2 and 5 and after a final filter of the EERC multicyclone system, so the ash was aerodynamically sized as it was collected. Gas velocity through the cyclones was held constant at both pressures for all tests, thus the aerodynamic diameters of the particles collected were greater than 10 microns for Cyclone 2, between 1 and 10 microns for Cyclone 5, and less than 1 micron on the filter.

To determine the efficacy of the kaolin additions in gettering, the weight distribution of elements among the different size ranges must be used. Figure 3.4-12 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. Results for the pressurized tests are in one graph, and the other graph gives the results 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 points represent data, from left to right, for the larger cyclone (>10 microns), the smaller cyclone (1–10 microns), and the filter (<1 micron).

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 and sodium were bimodally distributed. It is believed that the sulfur was present primarily as calcium sulfate in the largest particles and as sodium sulfate in the smallest particles. The distribution of sodium shows that about $\frac{1}{2}$ of it is gettered by the larger ash particles, most likely as sodium silicates and sodium aluminosilicates, while the other half is in a vapor phase, condensing as submicron sodium sulfate particles during sampling.

Pressure has little effect on the size distributions of the elements except for chlorine, which shifts 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 more of the chlorine condensed from the gas phase upon cooling at higher pressure than at atmospheric pressure. The effect is much stronger in the raw coal case than when kaolin is added, possibly because in the raw coal case more sodium vapor is present to permit the condensation of sodium chloride, as well as sodium sulfate, in the smallest particles.

When kaolin is added to the system, sodium and sulfur are strongly shifted from the smallest to the larger particles at both pressures. 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, both at

Cluster order is Cyclone 2, Cyclone 5, filter.

(A)

Cluster order is Cyclone 2, Cyclone 5, filter.

(B)

Figure 3.4-12. The weight percent of each element collected in each size fraction for the tests of kaolin as an alkali getter in the A) atmospheric and B) high-pressure tests.

atmospheric and higher pressures. Most of the sodium was shifted to the 1- to 10-micron size range, which is also where the kaolin is concentrated. The shift in predominant sulfur content from the smallest to the largest size range indicates the sulfur did not follow the sodium, and implies that the shifted sodium was chemically combined with the kaolin, probably during the high-temperature zone. It also implies that the kaolin did not merely serve as a condensation surface for sodium sulfate. Since much of the sodium was removed from the gas phase and was not available to combine with the sulfur, the sulfur shifted to the largest size range by sulfating additional quantities of the calcium-rich particles. This effect also accounted for the shift in chlorine when kaolin was added at higher pressures. However, at atmospheric pressure, the addition of kaolin had no effect on the distribution of chlorine because most of it stayed in the vapor phase even during quenching.

Computer Modeling of Gettering Efficiency

To determine the best way to add a getter to a system, it is helpful to determine the maximum equilibrium efficiency of the getter and to compare that value to a measured value for a given addition method. If the calculated equilibrium efficiency matches the experimental, then improvements in efficiency are not possible, unless some method of superequilibrium absorption can be devised. Figure 3.4-13 shows the total equilibrium concentration of all vapor-phase sodium-containing species calculated by the TEACH code to be in the products of combustion of Spring Creek coal, as functions of temperature and the kaolin-to-coal ash ratio. The data were calculated on a dry coal and dry air basis, assuming 20% excess air used for combustion. Chlorine was not included in the input data, and a plot at higher pressures was not made, because the experimental data showed that the effect of kaolin addition on chlorine concentration was significant at 109 psig, while it was not significant at atmospheric pressure.

The graph shows that the calculated total, vapor-phase sodium concentration at just below 1500°C (such as in the experimental work) was approximately 310 ppm (by weight). Calculations of the mass of vapor-phase sodium, based on the assumption that the submicron sodium measured in the PDTF tests came from vapor-phase sodium hydroxide, indicated that 480 ppm (by weight) was in the vapor phase in the PDTF, showing that the calculated was off by 35%. Also, the calculations illustrated in the figure indicated that approximately one-half of the vapor-phase sodium species could be gettered by the addition of kaolin at the kaolin-to-ash ratio of 0.5. This amount is approximately the same as that measured in the tests, showing that simple mixing of the kaolin with the coal was sufficient to provide the maximum possible equilibrium absorption of sodium species. The graph shows that at lower temperatures and with greater levels of kaolin addition, less sodium was present at equilibrium in the vapor phase. At 1000°C and with no kaolin added, a situation such as that near a hot-gas cleanup device in a system burning Spring Creek coal, approximately 50 parts per billion by mass (ppbm) sodium species were at equilibrium in the gas phase, primarily as sodium hydroxide and sodium sulfate. This amount is double that presently permitted by some high-efficiency turbine manufacturers for the inlet to the turbine. However, at a kaolin addition rate of one-half of the ASTM ash rate, the vapor-phase sodium species drop to 13 ppbm at 1000°C. They stay near this level even to 1300°C, when kaolin is added at the same rate as the ASTM ash.

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Figure 3.4-13. The calculated concentrations of vapor-phase sodium species versus temperature and ratio of kaolin added to ASTM ash.

The peak at low kaolin additions and 1170°C was caused by a maximum in vapor-phase sodium hydroxide amounts, followed by a threefold reduction in its concentration at 1300°C, then a rapid rise at higher temperatures. Coincident with the drop in sodium hydroxide amounts is a shift in condensed-phase species from sodium sulfate and albite ($\text{NaAlSi}_3\text{O}_8$) at lower temperatures, to nepheline (NaAlSiO_4) above 1300°C. The peak at 1170°C was caused by an insufficient amount of silica in the system to condense all of the vapor-phase sodium, since the Si:Na ratio was only one at the higher temperatures but was three at lower temperatures. As kaolin was added, though, the peak at 1170°C disappeared because sufficient silicate became available. This result is preliminary at present and is being confirmed in the literature of experimental data.

Conclusions

Experiments with kaolin as an alkali getter at atmospheric and pressurized conditions showed that it can effectively getter about one-half of the sodium species from the vapor phase when added in a kaolin-to-ash ratio of 0.5. The kaolin chemically adsorbed the sodium and did not simply act as a condensation site for sodium sulfate and hydroxide. The kaolin addition also shifted the sulfur concentration to larger particles at both atmospheric and pressurized conditions and shifted the chlorine concentration to larger particles at pressurized conditions. At atmospheric pressure, much of the chlorine was believed to have stayed in the vapor phase upon quenching.

Thermodynamic equilibrium modeling of sodium gettering showed that under the conditions tested, simple mixing of the kaolin with the coal was sufficient to provide the

maximum equilibrium amount of gettering. The calculations also showed that additions of 1 part kaolin per 1 part ASTM ash were sufficient to getter enough sodium species to keep their concentrations below the most stringent requirements proposed by turbine manufacturers, at temperatures of up to 1300°C. Additions of 0.5 part kaolin to 1 part ash would keep the sodium species below required levels at 1000°C.

Literature Survey on Materials Knowledgebases

Background

The principal motivation of this survey of knowledgebases arose from the need to address issues of the structural and chemical stability of the materials used in hot-gas cleanup devices. Since in many cases, the power generation systems demand high performance from materials that are, as yet, undeveloped, the establishment of a knowledgebase of the chemical and physical properties of materials and the interactions that they may undergo with the products of coal combustion will impact significantly on all aspects of coal combustion. Once the construction of the knowledgebase is complete, a multitude of design, performance, and optimization issues can be resolved ranging from the solution of task-specific problems to the comparative assessment of overall design strategies.

Over the last few years, a number of critical reviews (168–170) have identified technologies of strategic importance. These include materials, biotechnology, energy, environment, aeronautics, information management, and computing. To support the full range of these nationally critical technologies, provide an efficient, cost-effective research and development infrastructure, and manage the massive corpora of extant and emerging information from heterogeneous and distributed data sources, fundamentally new and considerably more powerful data management systems are required. Fortunately, database management systems have undergone significant advances and tremendous growth during the last two decades (171, 172). The emergence and development of new disciplines and technologies such as fuzzy logic (173), expert systems (174), object-orientation (175), neural networks (176), virtual reality, genetic algorithms (177), and chaos (178) have resulted in fundamental conceptual and epistemological shifts regarding knowledge and data, their representation, management, visualization and analysis. The construction of extremely intelligent and powerful computing systems or *knowledgebases* that provide an almost oracular interface to information and its consumption is not only feasible but imminent as well (179).

The section below discusses knowledgebases in the context of materials research and development. In the subsequent section, the key areas of materials research that are critical to ensure expertise in a materials knowledgebase are described. The following section (Software Resources), lists some of the computational software packages related to materials and their properties. A complete list of the literature cited is provided in the reference section of this report.

Knowledgebase

The contrast between databases and knowledgebases is analogous to the contrast between information and intelligence. Although what is considered data in one context can be interpreted as knowledge in another and vice versa, a knowledgebase contains, in

addition to conventional textual and factual data, domain-specific *knowledge* that is represented either in the form of *frames* (180), *production rules* (181, 182), or *declarative clauses* (183, 184). The concept of a knowledgebase has grown from the artificial intelligence culture and is thus used to denote the knowledge representation structure over which the logical inferences are performed (185, 186).

In general, the knowledge embodied in a knowledgebase is represented using a complex set of structures and operators similar to the object-oriented paradigm such as *type* or *class* schemes, *multiple inheritance*, *polymorphism*, and *operator overloading* (175). This may be contrasted with the simple record structures used in conventional databases. From the database perspective, knowledgebases extend the functionality of traditional systems by providing services comparable to any general-purpose application language system. Additionally, they also eliminate the *impedance mismatch* that occurs in the traditional host-and-embedded-language organization of databases, thereby permitting more extensive query optimization including data flow analysis. Thus, knowledgebases provide a rich data model capable of capturing and representing complex and intricate relationships such as those that occur in the real world and especially in the materials arena.

The current 'knowledge' regarding materials exists primarily in the form of tabulations of specific properties or processes. Indeed, such materials property compilations have been in existence since the advent of paper and the printing press. The genesis of machine-readable or computerized materials properties databases occurred during the mid-sixties. Today, approximately 1000 computerized, publicly-accessible large materials databases exist. These range from compilations of thermodynamic properties of complex chemical compounds to welding procedures, weld qualification, and performance properties of welds. An overview of some of the more recent materials databases is given in Table 3.4-5.

In contrast to other databases or database management systems, materials and materials property databases are very intricate and present some challenging design and implementation problems (187-190). In view of the tremendous complexity of materials, almost all descriptions of them are approximations of varying degrees of accuracy. Despite this, the spectrum of such approximations ranges from the microscopic to macroscopic, image to pattern, static to dynamic, deterministic to probabilistic, instantaneous to long-term, phenomenological and empirical to theoretical, and numerical to symbolic. The semantic content of materials information is thus best entrusted to a system wide *data dictionary* or *thesaurus* (191) that can be used to introduce classifications based on the requirements of design, fabrication, microstructure, property, performance, and test method. In addition, a thesaurus can also be used to add value to the data in other ways such as extracting features from a microstructural image or performing statistical analysis on a dataset.

Issues of materials design, performance, and test methods also raise some additional problems. Normally, the designer uses examples of past designs with good or bad experiences that refer to well-established industrial standards, then evaluates, modifies, or improves them according to the design requirements. Thus a history of design cases is needed, together with the capability to conduct case-based reasoning. Further, since materials performance is determined after quantitative evaluation of real service conditions, dynamic and asymptotic approaches to materials data along the process is

TABLE 3.4-5

Selected List of Materials Databases

Database	Description
ABCUP	Critically evaluated phase equilibria data on 13,000 phase diagrams (192)
ACTIS	Critically evaluated tribological and performance data (193, 194)
ADEP	Ceramics and ceramics properties (195)
ALUSELECT	Engineering and technical property data for aluminum alloys (196)
BEILSTEIN	Structural properties of organic (heterocyclic) compounds (197)
C&HTC	High-temperature corrosion data on metallic alloys and intermetallics (198)
CIAC	Engineering and technical data on advanced ceramic materials (199)
CETIM	Engineering properties of metals, plastics, composites, and adhesives (200)
COMETA	Common and engineering properties of metals (200)
CORROSION	Corrosion data on carbons, metals, plastics, and rubber (197)
CRYSTMET	Evaluated crystallographic data on metals and intermetallics (197)
COR*SUR	Corrosion rates of metals, polymers, composites, and thermoplastics (201)
DIPPR	Data on commercially important chemicals (202, 203)
DOW-MEC	Physical, thermal, rheological, and electrical data on polymers and plastics (204)
EMIS	Electronic and semiconductor properties (197)
F*A*C*T	Thermodynamic data for equilibria calculations (205)
HDATA	Hydrogen-materials interactions data (200)
HEILBRON	Physical and chemical data on organic compounds (197)
HIGHTEMP	High-temperature tensile and creep properties of steels and steel alloys (206)
HTM-DB	Corrosion and related mechanical properties of high-temperature materials (200)
HTMIAC	Laser irradiation data on metals, structural composites, and coatings (207)
ICSD	Inorganic crystal structure data (197)
INFOS	Cutting value (turning, drilling, milling, etc.) data of metals (200)
IVTANTERMO	Thermodynamic data on inorganic substances (208)
JANAF	Thermodynamic data on organic and inorganic compounds (197)
MATUS	Mechanical, and processability data on plastics, metals, and composites (200)
MDF/1	Mechanical and physical properties of ferrous and non-ferrous alloys (200)
MIAC	Engineering properties of monolithic metals, alloys, intermetallics, and coatings (209)
MIL-HDBK-17	Polymer-matrix composites data (210, 211)
MMCIAC	Engineering properties of metal-matrix composites and laminates (212)
NISTCERAM	Thermal and mechanical properties of silicon carbides and nitrides (197)
NISTKIN	Gas-phase reactions kinetics data (213)

TABLE 3.4-5 (cont.)

Database	Description
NMPD	A distributed database network server, it currently provides access to sections of MIL-HDBK-5 (the design manual of the U.S. Aerospace industry [214]), sections of ASMH, (the Aerospace Structural Metals Handbook [215]), and STEELBUF, a database of more than 20,000 individual toughness tests of more than 50 steels (216)
PDFC	Phase diagram data (217, 218)
PERITUS	Metals and plastics data for CAD applications (200)
POLYMAT	Properties of plastics (200)
RUST	Engineering and test values of metallic and nonmetallic coupon corrosion (219)
SCD	Thermal, mechanical, and corrosion data on SiC and SiN (220, 221)
THERMODATA	Thermodynamic data on complex chemical compounds (200, 222)
TRCTHERMO	Thermodynamic data on over 7000 substances (197)
WIN	Expert system on welding processes, procedures, and weld data (223)

important, in addition to the capacity to perform simulations of structural and microstructural evolutions under performance conditions. Finally, to comply with the design and performance optimization requirements, the ability to undertake parametric studies is also essential.

Materials Research

Materials property data and manufacturing methods are the raw materials of a wide spectrum of processes and design operations. The development, design, planning, and operation of processes in almost any industry require a large amount and wide diversity of basic materials data. Often, the properties and attributes of interest are unique to the process or industry in question. Spacecraft navigation systems for instance need low weight, high strength materials (224). On the other hand, heat exchangers in direct-fired power generation systems require high-temperature materials that are also resistant to the highly corrosive, hot exit gas and particulate ash streams (225). To provide the design engineer with the most appropriate material, vast amounts of money are spent on the analysis and characterization of old and new materials every year. For instance, the U.S. National Science Foundation (NSF) funded about \$1.3 billion of materials-related research in 1993 (226), while the German chemical company BASF alone spends about DM 8 million every year in thermodynamic and physical property measurement and compilation (227). But, the design engineer is still unable to effectively utilize this data because the generated data is not communicated in a timely fashion. Another reason for not using the data is that, even if the information reaches the process designer on time, it is often in a form that precludes its immediate usage in any design calculations. Thus, a significant interface problem exists in communicating the laboratory or research results to the end user (228).

In the past, materials research usually represented a relatively small portion of the overall costs of any industry. Prior to the advent of plastics and polymers, many of the

common materials such as wood, bricks, glass, ceramics, copper, iron, tin, lead, gold, etc., had been in use since ancient times and their processing and manufacturing properties were quite well understood. Now however, the selection of materials is a critical, time consuming, and expensive process in all types of product development. In some cases the choice is clear-cut and easy to make as in selecting between steel and aluminum. In other cases, the design requirements interact in various ways to create multiple, and often conflicting, choices requiring the services of materials experts to generate viable choices. Premature decisions, inaccurate materials property data, or even subtle differences in comparable materials can often result in costly and catastrophic errors (229-232). The task is further complicated by the proliferation of material types and grades and by the ever increasing demands on optimization of products with respect to weight, cost, energy requirements, environmental impacts, and so on (233).

The search for new materials that have new and improved properties is another time consuming, costly process but a very important area of materials research. The exponential growth of the combinations of new materials that can be engineered from the periodic table of elements can be seen from Table 3.4-6 (234). Likewise, Table 3.4-7 shows the proliferation of intermetallics of two possible phases that result from a given list of 89 elements (234). It is apparent from these two tables that because of the explosion in the number of possibilities for compounds of higher arity, manual characterization of these will be prohibitively expensive, and less expensive and more efficient methods are urgently needed. Such methods must be capable of not only providing materials properties on demand and at a fraction of the cost and time needed by conventional means but must also have the capacity to intelligently update and modify themselves based on the existing and new corpus of materials data.

TABLE 3.4-6

Actual versus Maximum Number of Compounds Grouped by Elemental Composition

Arity of Compound	Maximum Number	Experimentally Known Systems	Experimentally Known Systems, %
Unary	100	100	100
Binary	4,950	4,000	81
Ternary	161,700	8,000	5
Quaternary	3,921,225	1,000	< 0.1

TABLE 3.4-7

Actual versus Maximum Number of Two-Phase Intermetallic Compounds

Arity of Compound	Estimated Maximum	Number of Experimentally Known Systems	Compound Type of Experimental Systems, %
Unary	189	551	1.4
Binary	7,823	18,586	45.6
Ternary	227,128	19,597	48.1
Quaternary	4,800,000	1,928	4.7

Conventionally, the search for novel materials has been carried out primarily through two computational schemes. The first scheme is phenomenological in nature. It attempts to classify, establish orderings of, and impose similarity measures on materials that are expected to expose any underlying patterns or relationships between their structure and properties. This essentially taxonomic study of materials, or quantitative structure activity relationship (QSAR) as it is called, is based on a variety of symmetry and similarity principles (235). Some of these principles are *equivalence relations* (236, 237), *analogical and inductive reasoning* (238, 239), *complementarity* (240–243), and *scaling* (244–246). Table 3.4-8, adapted from (235), lists some of the applications of these similarity principles to chemistry and materials science.

Pattern matching and similarity studies have shown that there exist concrete quantitative relations between experimentally determined phase diagram structure, crystallographic data, and intrinsic physical and chemical properties of multinary systems and tabulated fundamental properties of constituent atoms or constituent functional groups (247, 248). The atomic properties or parameters of primary interest are pseudopotential radius (249), atomic number, valency, melting temperature (250), and electronegativity (249). The quantitative relationships that have been found include compound and noncompound formation in ternary systems (251), atomic environment (252), structure maps (253, 254), and structural relations (255–257), properties of high-temperature superconductors (258), high-temperature ferroelectrics (259), stable

TABLE 3.4-8

Applications of Similarity Principles

Year	Author	Similarity Application
1811	Avogadro	Avogadro's law
1819	Dulong and Petit	Law of specific heats
1830	Berzelius	Isomerism
1840	Berzelius	Allotropy
1845	Gerhardt	Homologous series
1869	Mendeleev	Periodic table
1874	Le Bel and van't Hoff	Stereoisomerism
1894	Fischer	Drug-receptor complementarity
1913	Soddy	Isotropy
1921	Ruzicka	Isoprene rule
1925	Franck	Franck-Condon principle
1934	Hückel	Structural stability
1938	Rice and Teller	Rice-Teller principle
1955	Hammond	Transition states
1964	Hansch and Fujita	Structure-activity principle
1964	Woodward and Hoffmann	Woodward-Hoffmann rules
1977	Hine	Nuclear motion
1980	Ugi et al.	Chemical distance
1980	Carbó et al.	Molecular charge
1985	Mezey	Molecular shape group

quasicrystals (260), high-weldability materials (255), high melting temperature, low-density materials (261), materials with tailored electrical conductivities (262), and materials with tailored melting temperatures (263).

As remarked earlier, the number of possible compounds of higher arity grows exponentially. The search for patterns and regularities in large sets of experimentally or otherwise determined data, thus, must be conducted extremely efficiently. Conventional pattern recognition methods require unacceptably long times when presented with large data sets. In analyzing compounds of higher arity, development of strategies is needed to investigate the most promising materials first out of the unlimited number of materials that are theoretically possible. Systems and materials that exhibit regularities enable us to make predictions that can be used to optimize their properties. Violations to such regularities may lead us to the discovery of new, exotic materials. The techniques for interpolating and extrapolating properties of materials from the vast array of experimental data need to be extended. The role of regularities and predictions in material science can be best summed up by the role that theorists play in exploring the complex world of nature: "The best a theorist can hope to do is point an experimentalist in the right direction, and this best [is] done by suggesting what directions to avoid" (264).

The second computational scheme used in the search for new materials is *ab initio* or first principles quantum mechanical calculations. *Ab initio* calculations rely on the advances in condensed matter physics and supercomputing power to predict the structure and property of materials (265). Starting with the information on the chemical composition of the material, and using advanced computing techniques, the predictions of a variety of properties (structural, electronic, optical) are now possible (266–271). Examples of such predictive calculations include the electronic structure studies of the 7 x 7 reconstruction of the surface of silicon (272), the elucidation of the details of the mechanism of activation of the microporous catalytic system Ni-zeolite (273), and the prediction (prior to observation) of the elastic constants and equation of state of the high-pressure, perovskite-related polymorph of MgSiO_3 , which comprises a major component of the lower part of the earth mantle (274).

It is useful to classify *ab initio* calculations into two categories, namely, *simulations* and *electronic structure determinations*. Simulations are based on an effective potential which subsumes knowledge of electronic structure into a numerical or analytical function describing the variation of the total energy of the system with the position of the nuclei. Such potentials may then be used in energy minimizations (EM), and in Monte Carlo (MC) and molecular dynamics (MD) simulations. Energy minimization allows an economical determination of minimum energy structures for crystals, defects, surfaces, and sorbed molecules but is limited by the static lattice approximation (275). MC methods, usually based on some variant of the Metropolis algorithm (276) are well-suited for generating thermal equilibrium ensembles of configuration states and for studying temperature dependence (277). MC simulations have been used to develop equations of state, determine fluid phase equilibria, explore Ising systems, analyze thermal annealing of vacancies and interstitials in irradiated metals, compute criticality and phase transition parameters, and so on (277–280). MD simulations yield full dynamical details by integrating the dynamical equations of motion and have gained in popularity since the advent of high-speed computers (281, 282). MD simulations have been used to study liquids (283), molten salts (284), superionic solids (285), Alder transitions, relaxation dynamics near glass transitions, and crystal-to-smectic transition in liquid crystals (286),

friction, wear and lubrication phenomena (287), Poisson ratios for fcc and other lattices (288), diffusion coefficients (289, 290), shear viscosities (291, 292), thermal conductivities (292), sintering (293) and so on. The only disadvantage with MD simulations is the limited time period of the simulations. A nanosecond is about the maximum time period that even the most advanced supercomputers currently in existence can handle. Nevertheless, the simulation methodologies are by now well-developed and well-established, and the crucial factor limiting their accuracy and further progress concerns the accuracy of the interatomic potentials.

Electronic structure determination, in which the Schrödinger equation is solved to some level of approximation, is the second class of methods used in materials studies. Essentially two main classes of approximation schemes exist for solving the Schrödinger equation (294–296): systematic corrections to the Hartree-Fock (HF) model, which neglects electron–electron correlations, and density functional theory (DFT). HF methods have dominated in computational chemistry until now, and the techniques employed range from semiempirical, in which matrix elements are approximated using empirical data or ignored, to *ab initio* in which all integrals above a threshold are evaluated analytically or numerically. The semiempirical scheme may be used to study systems with fairly large numbers (> 100) of atoms, while the *ab initio* technique is primarily used to refine models developed using the semiempirical approach. HF calculations can also be performed on clusters (with embedding procedures in which the cluster is surrounded by some approximate representation of the rest of the system) or on periodic arrays of atoms or lattices; in all cases, the computing power scales as N^6 or higher, where N is the number of electrons in the system. HF methods have the advantage that the approximations used have a firm basis in the physics/chemistry of the system and thus are well understood. Also, a considerable body of experience, gained from molecular quantum chemistry, establishes suitable basis sets.

DFT provides an alternative approach to electron-structure determinations. The central object of computational interest here is the electron density distribution of the system rather than its wave function (297–299). The local density approximation (LDA) techniques of DFT, which have been extensively used in the solid-state physics community, are now increasingly recognized as important for computational chemistry and materials science in general. The essence of the local density approximation is the use, in evaluating the total energy of the system, of expressions for the exchange and correlation energy that are appropriate to the electron gas of uniform density. DFT methods possess the distinct advantage that the computational requirements scale only as N^3 (N is the number of electrons in the system), which is much more favorable than the N^6 or N^7 requirements of HF-based methods. In addition, electron–electron correlation effects are included directly in DFT, whereas HF methods must be extended to include configurational interaction terms, although correlation effects may be incorporated via a density expression following an evaluation of the HF wave function. DFT offers clear advantages for larger molecules; it is the preferred method for crystalline and amorphous solids and has been successfully applied to dozens of crystals to yield structural and electronic information including that for high-pressure and superconductive systems (300, 267).

One of the most useful by-products of high quality *ab initio* calculations is the construction of reliable parametrizations of *interatomic potentials* (236, 301–303). Indeed, for many problems it is more appropriate to use the electronic-structure determination

techniques to construct the interatomic potentials rather than undertake the electron-structure calculation directly. Although the use of ab initio methods for this purpose is not new, the accuracy of the results obtained make these invaluable to materials research since, as remarked earlier, interatomic potentials are central to performing any EM/MC/MD simulations as well as to other applications such as analysis of vacancies and lattice defects (304–307) and fracture and grain-boundary modeling (308, 309).

In addition to the more well-known *Mie* (310), *Lennard-Jones* (311), *Morse* (312), and *Born-Mayer* (313) semiempirical, two-body potentials, *pseudopotentials* (314, 315), and the more recent *embedded atom potentials* based on density functional theory (316, 317) also exist. All of these potentials suffer from drawbacks in one form or another. For instance, the Lennard-Jones and Morse potentials satisfy the Cauchy relation between the compressibility and the shear constant; the Born-Mayer model suffers from its inability to define the sample volume unambiguously; pseudopotentials are long-ranged and undergo Friedel oscillations (318), while the DFT-based embedded atom potentials, although the most promising, are computationally expensive compared to the other two-body potentials. These drawbacks are partly responsible for the lack of successful models of some systems such as electrolytes in mixed solvents, multicomponent liquid mixtures, and strong-interaction materials (319). Addressing the problems raised by the current two-body interaction models and developing three-body and higher-order interaction terms are two other fundamental and vigorous branches of materials science research.

Software Resources

TABLE 3.4-9

Selected List of Materials Knowledge Software Tools

Program	Synopsis
ALPID	Finite element modeling (320, 321)
CASCADE	Lattice and defect simulations (322)
CRYSTAL	Periodic HF electron-structure calculation (323)
FLEX II	Dislocation core simulation (324)
FUNGUS	MD package for the simulation of superionic solids (285)
HADES	Defect simulation in crystals (325, 326)
HELL	Grain-boundary growth simulation (327–329)
KWM	Gas-phase viscosities, thermal conductivities, diffusion coefficients (330)
MARC	Finite element modeling package (331)
MORATE	Rate constants of gas-phase reactions (332)
PLUTO	Lattice energies, elastic, and dielectric properties (275)
PARAPOCS	Lattice free-energy minimization (333)
WMIN	Static lattice energy calculations (334)

Bench-Scale Measurements

Originally a probe system that could be used for long-term ceramic filter testing in the pressurized drop-tube furnace (PDTF) was proposed. The probe system was originally proposed because it would be a low-cost method to expose ceramic filter elements to coal ash under high-temperature and high-pressure conditions over long operating periods. However, because of difficulties in controlling the temperature in the zone of the furnace where the ceramic filter would be operated, and since the high workload on the PDTF makes it difficult to schedule long operating periods devoted strictly to ceramic filter testing, EERC personnel do not feel that assembly of a probe system for use in the PDTF would be appropriate at this time. Alternative approaches have been considered by EERC personnel and discussed with the DOE-METC Technical Project Monitor. Alternative approaches considered include building a bench-scale filter vessel to be used with bench-scale pressurized combustion and gasification reactor systems. A second option would involve building an extractive sampling system to test small filter elements in conjunction with the operation of any EERC combustion or gasification system. At this point in time, the preference appears to be the design and construction of a bench-scale filter vessel that could be used in conjunction with the bench-scale pressurized fluid-bed reactor (PFBR for combustion) and the continuous fluid-bed reactor (CFBR for gasification/pyrolysis). Also, the unit should be designed to be used as a slipstream device on other pressurized combustion and gasification systems and atmospheric combustion systems at the EERC.

The basic design criteria for the bench-scale filter vessel include an operating temperature of 1450°F, an operating pressure of 150 psig, process gas flow rates of roughly 35 scfm, filter face velocities of 6 to 12 ft/min, a heated back pulse, and external heating. A conceptual drawing should be available for review by the DOE-METC Technical Project Monitor in January 1994.

Pilot-Scale Measurements

Modifications to sampling equipment to be used for particulate and trace element sampling in support of the transport reactor demonstration unit (TRDU) operation continued at a limited level during the past year. Specific activities focused on final design and assembly of a sampling system, selection of an appropriate location for the sample port on the TRDU, and design and installation of the sample port. Upon further review, additional design modifications will be necessary before the sampling system will be ready for testing. Critical issues center around effective component heating and cooling as well as safety concerns with respect to insertion and removal of probes from a hot, pressurized environment. One complete sampling system should be assembled and ready for use in March during a scheduled TRDU operating period. A second sampling system will be assembled once successful performance of the first system has been demonstrated.

Reassembly of the hot-gas test loop has been delayed, pending the status of and future operating plans for the TRDU. Work on the hot-gas test loop will not begin until both these issues have been resolved.

A new activity was added in September 1993 to Task 3.4, Subtask 3.4.5 Hot-Gas Cleaning. The purpose of the new activity is to initiate an effort to design and construct a hot-gas filter vessel to be operated in conjunction with the TRDU. Work on this activity

will not begin until the operational status of the TRDU has been adequately demonstrated to the DOE-METC Technical Project Monitor and permission is received to proceed with the task.

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TASK 3.0 ADVANCED POWER SYSTEMS

Subtask 3.6 Technology Assessment

INTRODUCTION

The United States has invested heavily in research, development, and demonstration of efficient and environmentally acceptable technologies for the use of coal. This effort, involving the U.S. Department of Energy (DOE), as well as numerous U.S. industrial groups, has placed U.S. technology in a leadership role worldwide. The Energy & Environmental Research Center (EERC) has been a partner with industry and the Department of Energy in many of these ventures, particularly those focused on low-grade coal resources.

Recent discussions with key groups in the Czech Republic, including the Czech Mining Association, have identified the following key needs:

- Identification of proven technologies that would be cost-effective options for the utilization of native Czech brown and black coals, while at the same time being good environmental performers.
- The necessity that all technologies identified meet environmental objectives consistent with the United States Clean Air Act and other American environmental laws.
- Identification of costs associated with the various technology options and possible financing alternatives, including financial approaches, possible funding institutions, and business configurations.

The U.S. has the opportunity to use its leadership position to market a range of advanced coal-based technologies on the international market. The Czech Republic offers an excellent opportunity for the export of high-technology value-added equipment and services by U.S. industry.

OBJECTIVES

The overall objective of this project is the development of opportunities for U.S. clean coal technology in East Central Europe. Special attention is given to opportunities for implementation of U.S. clean coal technology in the Czech Republic.

ACCOMPLISHMENTS

Work has gone forward in two areas as part of the EERC initiative to commercialize U.S. clean coal technology in the Czech Republic. First, information has been gathered on specific opportunities for commercialization of U.S. technologies in the Czech Republic. This has involved communication with knowledgeable people in both Czech government and industry. These individuals, as well as sources available within the U.S., have been

used to gather information on current and planned activities and perceived needs, as well as on the quality and quantity of available resources. This information is being evaluated to determine the most promising options for commercialization of U.S. clean coal technologies in the Czech Republic.

The second principal area of activity involves the introduction of U.S. technology to the Czech Republic. Two activities are planned: the Second International Conference on Energy and Environment: Transitions in East Central Europe, as well as two workshops to be presented in conjunction with the conference. The workshops are entitled "Least-Cost Economic Power Generation in East Central Europe" and "Production and Utilization of Ecological Fuels from East Central European Coals."

Work is progressing on both activities. Outlines have been generated for both workshops. These outlines have been reviewed with an EERC Advisory Council of East Central Europeans and with the U.S. Department of Energy. Their comments have been incorporated, resulting in the following tentative agendas.

Least-Cost Economic Power Generation in East Central Europe

Session 1. Summary of Status and Needs

- Position of Coal in Relation to Oil, Gas, and Nuclear Power in East Central Europe
 - Existing facilities and capacity
 - Projected demand
 - Projected changes in power sources (fuels)
- Status of Restructuring of the Power Industry in East Central Europe
 - Organizational structures – power companies
 - Financial mechanisms – e.g., joint ventures, etc.
 - Legal framework, including privatization issues
 - Regulatory structure – prices, dispatch, environment
- Environmental Goals and Objectives
- Competitive Economics of Fuel Choices (i.e., brown coal versus gas)
- Discussion

Session 2. Improvements in Availability and Life Extension of Existing Units and Impacts of East Central European Coal Properties

- Historic Problems Burning High-Moisture, High-Ash Coals
- Effects of Coal Ash Properties on Availability
- Coal Handling and Storage

- Availability and Efficiency Improvements in Existing Units Without Life Extension
- Ash Fouling, Corrosion, and Erosion in Conventional Boilers
- Technical Feasibility and Economics of Life Extension
- Barriers to Waste Utilization and Disposal
- Discussion

Session 3. Retrofit and Repowering for Emissions Control and Efficiency

- Coal – Effective Retrofits for Emissions Control
 - NO_x
 - Flue gas desulfurization (FGD)
 - Electrostatic precipitator (ESP) rehabilitation
- Sulfur Control – Coal Cleaning versus FGD
- Effect of Ash Properties on Pollution Control Systems (e.g., ESP, baghouse, and FGD)
- Repowering Using Fluidized-Bed Combustion Technology
- Conversion to Combined Cycle Gas Turbine with Gasification to Come Later
- Ash Behavior in Repowered Systems
- Discussion

Session 4. Opportunities for Partnerships

- Least-Cost Planning and Analysis
- Financial Options and Requirements for Obtaining Capital
- Government Policies Affecting Foreign Investment
- A Case Study of a Successful Partnership
- Panel Discussion with Prepared Questions

Production and Utilization of Ecological Fuels from East Central European Coals

Session 1. Markets (Current and Projected), Environmental Objectives, and Economics

- Overview
 - Market trends and persistence in competition with natural gas
 - Economic and price factors
 - Environmental requirements and related fuel specifications
 - Technical parameters involved in meeting specifications
- Selected Country Perspectives
 - Current production capacity and methods
 - Utilization in industrial, commercial, and residential applications
 - Pending changes in commercial practice (new projects and changes in technology)
 - Future requirements in terms of product quantity and quality
 - New technology under development
- Poland
- Czech Republic
- Bulgaria
- Germany (formerly East)

Session 2. Technologies

- State-of-the-Art German Briquetting Technology
- Gravimelt Czech Application
- K-Fuel
- SGI (Encoal)
- FMC Formcoke®
- Polish/U.S. Briquette Project
- Cold Press Briquetting (assumed to involve biomass admixture)
- Calcium Silicate-Bonded Metallurgical Coke

Session 3. Advanced Methodologies

- Char Production Methods for Producing Eco Fuels
- Correlation of Coal Properties to Char, Briquette, and Utilization Characteristics
- Survey of Briquetting Parameters and Binders
- Strategies for Sulfur Capture
- Coal-Water Fuels (CWFs) for Briquettes or CWF

Session 4. Panel Discussion: Partnership Opportunities, Technology and Marketing

- A Review of Regional Opportunities for Producing and Exporting Ecological Fuels
- Recap of Presentations by Presenters
- Discussion with Prepared Questions

The Second International Conference on Energy and the Environment: Transitions in East Central Europe

The preliminary program for the Second International Conference on Energy and Environment: Transitions in East Central Europe was issued in December 1993. The conference is scheduled for November 2-4, 1994 with the workshop scheduled for October 31 and November 1. Topics in the program have been divided into two streams, entitled "Technical Issues" and "Socioeconomic Issues." Sessions on the following topics have been identified.

Technical Issues

- Conventional Energy Systems I – Economic Operation of Existing Energy Systems
- Conventional Energy Systems II – Boiler Emissions Control
- Conventional Energy Systems III – Retrofitting and Repowering
- Waste Management: Utilization
- Advanced Energy System Technologies
- Waste Management: Disposal

Socioeconomic Issues

- Moving to a Market Economy

- Capital and Financing
- Regulatory Issues
- Cost versus Benefits – Case Studies of Energy Systems
- Energy Resource Options
- Environmental Economics: Perception and Reality in Conflict

The task of identifying and securing presenters and session chairpersons for the conference is underway. Judging from the very enthusiastic response in the U.S. and in East Central Europe, we anticipate a highly successful conference.

APPENDIX 3.2-1

A NEW APPROACH TO CALCULATING COAL ASH VISCOSITY

AND

LOCAL STRUCTURE OF A LIGNITE COAL ASH SLAG AND ITS EFFECT ON VISCOSITY

A NEW APPROACH TO CALCULATING COAL ASH VISCOSITY

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A new approach has been developed for the prediction of coal slag viscosity in the case of phase separation below the temperature of critical viscosity. This phenomenon causes deviations from ideal viscosity as compared to unseparated slag of the same bulk composition. We discuss the cause of viscosity deviation in slags and introduce a new method of viscosity calculation that accounts for the structural changes in the slag as phase separation begins. It is assumed that the viscosity depends on the degree of polymerization of the slag and the dispersion of nuclei. Above the critical temperature, viscosity is calculated from both Arrhenian and configurational entropy models. Both models are modified as the base/acid ratio crosses a value of 0.2.

1. INTRODUCTION

In order to predict the bulk viscosity of liquid mixtures consisting of simple flow units, the Arrhenius equation can be applied. However, if the flow units become more complicated, as in polymerized silicates, and the number of volume-dependent degrees of freedom decreases, the Arrhenius approach may not be useful any longer. This led Gibbs (1960) to focus attention on the configurational entropy (S_{conf}) as the primary extensive variable affecting the liquid viscosities. Configurational entropy is the excess entropy of a liquid over that of the crystalline phase. S_{conf} tends to zero if viscosity reaches values in excess of 10^{13} poise. The connection between viscosity and the configurational entropy was formulated by Adams and Gibbs (1965) as follows:

$$\eta_{\text{conf}} = A \exp B/TS_{\text{conf}} \quad (T \text{ in K}) \quad (1)$$

where A is a preexponential factor and B is a constant containing a free energy barrier.

Most phenomenological models (Urbain et al., 1982) of silicate-based slag viscosity rely on finding an algebraic expression for viscosity as a function of ash composition and temperature expressed in terms of several constants. An example is an equation of the form:

$$\log \eta = \log C + 10^3 D T^{-1} \quad (T \text{ in K}) \quad (2)$$

where C and D are constants defined by the composition of coal ash. Many attempts (Hoy et al., 1965; Kalmanovitch and Frank, 1990; Jung and Schobert, 1992; Srinivasachar et al., 1993) were made to improve correlation of the experimental values with predicted ones using multiple linear regression analysis. However, as the temperature drops, a critical temperature is reached below which

the relationship is no longer linear. Much of the deviation is due to structural changes in the melt. Generally, structural changes are caused by the changes in the degree of polymerization of the melt resulting from phase separation and further formation of crystalline nuclei. This is observed by systematic increases of Arrhenian activation energy when the temperature decreases. Thus the overall viscosity-versus-temperature curve is quite sensitive to both the composition and structural changes of the melt.

Generally, melts can be classified as Newtonian and non-Newtonian liquids. Viscous flow of Newtonian melts requires the formation of a volume "hole" into which the flow unit moves when the hole exceeds some critical volume (Turnbull and Cohen, 1961). In this model, the transport of matter can occur as a jump of flow units. In an attempt to predict viscosity in the Newtonian region, an Arrhenius equation may be applied:

$$\eta = \eta_0 \exp [E/kT] \quad (3)$$

where η_0 represents zero-shear viscosity, also known as a preexponential factor, and E is an activation energy. Zero-shear viscosity in aluminosilicates is a structure-sensitive parameter. Thus this property can help to identify molecular properties, and it is needed to fit certain composition-based equations to experimental flow rate data. In addition, an activation energy is associated with local slag structure and its composition.

The temperature at which the flow changes from Newtonian to non-Newtonian is known as the temperature of critical viscosity (T_{∞}). As slags cool past T_{∞} , solid assemblies and less polymerized "residual slag" form (Nowok and Benson, 1992). Thus the slag is composed of a two-phase mixture. The temperature of critical viscosity can be viewed as a temperature at which the stoichiometries of polymers in the melt mimic those of crystalline phases that appear at the liquids. Below that temperature, the number of melt species may be compounded. These melt species will form crystalline phases as the temperature drops below the liquids (Burnham, 1981).

The viscosity of slag near T_{∞} may rise sharply due to a fraction of the volume being blocked from flow by solid particles. For this system, the viscosity depends on the volume fraction of dispersed solid assemblies (v), their shapes (disks, spheres, or rods), viscosity of "residual slag" (η_r), and the mutual hydrodynamic interaction of solid/melt and fractional processes (Goldsmith and Mason, 1967):

$$\eta_{\text{melt}} = \eta_r (1 + cv + dv^2) \quad (4)$$

where c and d are constants related to the shape of dispersant and solid/melt interaction, respectively. Prediction of slag viscosity using Equation 4 is difficult because of the large number of assumptions required concerning the variables.

In this paper we consider:

- The relation between the composition of ash slag as described by the base/acid ratio and its bulk viscosity in the Newtonian region, which may be expressed by an Arrhenius-type equation.
- The effect of local structure and composition on slag viscosity, using the configurational model of Adams and Gibbs (1965).

- Deviation from ideal viscosity determined by Arrhenius and Gibbs equations caused by structural changes of a melt at temperatures below T_{av} .

2. ASH SLAG VISCOSITY AND FACTORS AFFECTING CALCULATIONS OF RELATIVE VISCOSITIES USING AN ARRHENIUS EQUATION

Figure 1 illustrates the variation of activation energy with base/acid ratio for model glasses and ash slags. Data for model glasses were taken from literature (Bansal and Doremus, 1986; Clark, 1966; Dingwell and Virgo, 1988; Vores et al., 1985; Scarfe et al., 1983) and data for ash slags from our own measurements. Base/acid ratio was calculated from the composition of coal ashes:

$$\frac{\text{Base}}{\text{Acid}} = \frac{\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{FeO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{TiO}_2} \quad (5)$$

The non-linear regression parameters calculated for model glasses and for ash slags are 0.61 and 0.95, respectively. The lower value for model glasses is likely caused by the systematic increase of activation energy as the base/acid ratio drops below 0.2.

It becomes obvious that for these melts, the Arrhenian activation energy taken from the plot of linear relationship of E_{act} with base/acid ratio does not represent its original value. The new value of E_{act} may be obtained by introducing a dimensionless parameter "m" (Eq. 6):

$$E_{act} = [60 - 28(\text{base/acid})]^{1+m} \quad (\text{kcal/mol}) \quad (6)$$

FIGURE 1. Activation energy and base/acid ratio relationship on the model glasses and coal ash slags.

It is important to note that m is equal to zero for glasses and ash slags with a base/acid > 0.2 . For melts with a base/acid < 0.2 , the value of m increases with the decrease of base/acid ratio and thus modifies an Arrhenian activation energy. It is likely that the value of m is affected by the charge imbalance of Al^{3+} and Fe^{3+} ions, by alkali and alkaline earth cations, and by the entropy of mixing. Table 1 lists zero-shear viscosities and m values for calculations of ash slag viscosities.

Figure 2 demonstrates the temperature dependence of viscosity calculated for coal ash slag with a base/acid ratio = 0.18 using the two Arrhenius models previously discussed, as well as the Kalmanovitch-Urbain model. The accuracy of the predicted viscosity values is higher if activation energy correction is included. An ideal Arrhenian model may be used for slags with a homogeneous structure.

3. VISCOSITY-TEMPERATURE RELATIONS PREDICTED FROM CONFIGURATIONAL ENTROPY AND FREE ENERGY BARRIER IN ALUMINOSILICATE GLASSES AND COAL SLAGS

For most aluminosilicates the change of viscosity with temperature cannot be represented by an Arrhenius plot. Typically, the deviations from Arrhenian behavior increase with the temperature dependence of S_{conf} (Richet, 1984). For simple systems, the change of configurational entropy can be calculated from the integrated excess heat of capacity and/or directly from the viscosity data. We have selected a method that refers to viscosity data.

Figure 3 illustrates the variation of configurational entropy with temperature. Two regions of entropy change, above and below about 900°C, may be distinguished. At higher temperatures, the increase in S_{conf} makes possible the cooperative rearrangements of melt structure into different configurations. It is unlikely that this rearrangement may correspond with the glass transition temperature. Usually,

TABLE 1. Zero-Shear Viscosity (in Poise) and "m" Parameter for Coal Ash Slags

Base/Acid Ratio	η_0 ($\times 10^{-6}$)	"m" Parameter	Base/Acid Ratio	η_0 ($\times 10^{-6}$)	"m" Parameter
0.12	3	0.06	0.44	18	0.00
0.14	4	0.04	0.46	18	0.00
0.16	5	0.028	0.48	19	0.00
0.18	6	0.015	0.50	20	0.00
0.20	7	0.00	0.52	23	0.00
0.22	7	0.00	0.54	26	0.00
0.24	7	0.00	0.56	29	0.00
0.26	7	0.00	0.58	37	0.00
0.28	8	0.00	0.60	41	0.00
0.30	9	0.00	0.62	47	0.00
0.32	11	0.00	0.64	50	0.00
0.34	14	0.00	0.66	55	0.00
0.36	14	0.00	0.68	61	0.00
0.38	15	0.00	0.70	67	0.00
0.40	17	0.00	0.72	75	0.00
0.42	17	0.00	0.74	82	0.00

FIGURE 2. Calculated and measured viscosities for coal slag with base/acid = 0.18. The Arrhenian relation represented by curve (■) is calculated on the assumption that $m = 0$.

FIGURE 3. The variation of configurational entropy with temperature for selected silicate systems.

at the glass transition, the configurational entropy tends to zero, and viscosity reaches values in excess of 10^{13} poise. In silicates, S_{conf} is 2.99 ± 0.36 cal/mol per tetrahedrally coordinated silicon. If aluminum substitutes for silicon in the network, S_{conf} decreases to 1.98 ± 0.03 cal/mol. Also, iron and titanium may substitute for silicon and result in a S_{conf} change. At the present time, we do not know about S_{conf} change caused by iron and titanium in aluminosilicates. However, the ratio of $(SiO_2 + TiO_2)/(Al_2O_3 + Fe_2O_3)$ is not strongly affected by base/acid ratio. It varied from 1.11 to 1.80 for the 23 coal slags that we tested. Thus, the effect of ash composition on S_{conf} is minor, relative to the effects of temperature changes.

The free energy barrier and preexponential factor remain to be accounted for in viscous silicate glass and ash slag phenomenology. With increasing base/acid ratio, the free energy barrier is sensitive to melt composition, as is the Arrhenian activation energy. The barrier for glasses varies according to the following equation:

$$B = [29 - 28(\text{base/acid})] \quad (\text{kcal/mol}) \quad (7)$$

Equation 7 has been derived from the B versus base/acid ratio plot such as it has been proposed for an Arrhenius model (Figure 1). Unfortunately, our consideration of B in glasses is limited to a base/acid ratio between 0.1 and 0.6 due to the lack of experimental data. For aluminosilicate glasses, B ranges from 12 to 160 kcal/mol and usually increases with the degree of polymerization of the melt (Richet, 1984). The preexponential factor is expressed in poise and ranges between 15 and 30.

Figure 4 shows the calculated viscosity for model glass in the temperature range of 400° to 1400°C . Experimental data fit well to predicted data. This implies that calculated viscosities for model glasses, based on the configurational entropy approach, may also be used to produce reasonable structural models for silicate and aluminosilicate glasses in coal ash slags, which are quite sensitive to both glass composition and structure.

The B expression for ash slag is different from that for model glasses and is given as:

$$B = [36 - 10(\text{base/acid})]^{(1+m)} \quad (\text{kcal/mol}) \quad (8)$$

where the m factor has values similar to those in an Arrhenian equation if the base/acid ratio ranges from 0 to 0.2 (see Table 1). Also, the preexponential factor has different values, as shown in Table 2.

A comparison of predictions of the viscosity of ash slag with base/acid = 0.18 for this and previous methods is illustrated in Figure 5. The results indicate a good relationship between experimental results and applied models. This high accuracy between predicted and measured viscosities is only observed in ash slags with base/acid ratios below 0.2. For these systems, high viscosity does not allow the rearrangement of the melt structure to occur. Also there is not any significant difference between the modified Arrhenius and the Adams and Gibbs equations. Unfortunately, there is a deviation between predicted and measured viscosities in ash slags with base/acid > 0.2 that increases with base/acid ratio. Both relations bring the same uncertainty in predicted viscosity values.

FIGURE 4. Example of calculated viscosity based on the configurational entropy approach.

TABLE 2. Preexponential Factor A as a Function of Base/Acid Ratio.

Base/Acid	A	Base/Acid	A
0.14	35.0	0.39	2.5
0.17	22.0	0.43	1.5
0.18	11.0	0.47	1.5
0.19	4.0	0.51	1.2
0.26	3.0	0.57	1.2
0.32	2.5	0.61	1.2
0.35	3.0	0.64	1.2
0.37	2.0	0.73	1.0

4. DEVIATION FROM IDEAL VISCOSITY DUE TO STRUCTURAL CHANGES IN THE MELT

Many slags show deviations from ideal viscosities as they cool. The viscosities are usually somewhat larger than those calculated from Adams and Gibbs and/or Arrhenian equations as temperature is lowered. The larger values are believed to be due to blocking a portion of the slag volume from flow as a consequence of phase separation and nucleation. The tendency towards phase separation and nucleation increases with the decrease of the slag viscosity. The degree of nucleation is related to both composition and temperature. Of course, the rapid increase of viscosity with falling temperature effectively prevents nucleation. In those cases where the difference between measured and calculated viscosity ($\Delta\eta$) is the same for slags with the same base/acid ratio, the difference can be used to infer the degree of phase separation/nucleation in the slag.

FIGURE 5. Viscosity of ash slag predicted using configurational entropy approach and models discussed earlier.

The viscosity difference increases with base/acid ratio. This, however, appears to depend on the temperature of critical viscosity. Figure 6 illustrates the variation of critical viscosity with base/acid ratio derived from our viscosity results. In this sense, the problem of predicting viscosity for slag with suspended nuclei and/or particles as a function of temperature is to define the relation between $\Delta\eta$ and base/acid as well as $(T_{\infty}-T)$, where $T_{\infty} > T$. Also, the variation of temperature of glass transformation for some phases in coal slags with base/acid ratio is shown in Figure 6. Postulating that T_{∞} corresponds with nucleation and further crystallization of some phases, the increase of T_g implies the increase of viscosity. Figure 7 shows the change in $\Delta\eta$ as a function of $(T_{\infty}-T)(\text{base/acid})$. The formulation of T_{∞} and $\Delta\eta$ allows calculation of viscosity at temperatures below the temperature of critical viscosity. Thus the viscosity for nonideal slags may be given by the following equation:

$$\eta = \eta_{\text{conf}} + \Delta\eta \quad (9)$$

and finally:

$$\eta = \eta_{\text{conf}} + r(T_{\infty}-T)(\text{base/acid}) \quad (10)$$

where η_{conf} is given by Equation 1, and $r=9.2$ [poise/deg.].

Results of predicted viscosity for ash slags with and without structural changes are shown in Figure 8. No differences in viscosities are observed at 1300°C. It is clear that higher temperatures stabilize slag structure. Most of the deviation that occurs at lower temperatures results from structural changes. The predicted

FIGURE 6. Change of temperatures of critical viscosity and glass transformation in ash slags.

FIGURE 7. Relationship between viscosity difference and $(T_{cv} - T)$ (base/acid).

FIGURE 8. Log η -base/acid relations for ash slags calculated at various temperatures.

viscosities are in good agreement with those of commercially important aluminosilicates cited in literature (Bansal and Doremus, 1986). Usually, the viscosity at 1000°C is about 10^6 poise, and at 900°C about 10^8 poise.

5. ASH VISCOSITY AND FOULING TENDENCY

Ash particles with a liquid surface that strike heat exchanger tubes may stick and will sinter with time. The viscosity distributions of the ash particle surfaces play a major role in determining the fouling tendency of the ash. Figure 9 illustrates an example of slag viscosity changes with base/acid ratio at 900°, 1000°, and 1100°C. Coal ashes with base/acid < 0.2 have higher viscosities at a given temperature than those with higher base/acid ratios, which coincides with the decrease of the sticking probability and the fouling tendency of the ash. The sticking probability is inversely proportional to viscosity for a given particle mass and velocity.

6. CONCLUSIONS

A new approach to calculating coal ash viscosity represents a portion of our wide interest in physical properties of coal ashes and slags. Generally, the viscosity of the bulk material is a controlling factor for sticking phenomena, sintering and slagging propensities, corrosion of refractories, crystallization of ash slags, as well as wall heat flux. Thus the prediction of accurate values of bulk viscosity, in the range of temperature starting from the temperature of glass transition (T_g) up to about 1500°C, is important.

FIGURE 9. Log η -base/acid relations for ash slags calculated at fouling temperatures.

Both Arrhenian and configurational entropy models were employed to calculate bulk coal slag viscosity. Both models gave predictions that deviated from ideal viscosities below the temperature of critical viscosity (T_{∞}) due to phase separation and further nucleation. The differences between measured and calculated viscosities increased with base/acid ratio of coal ashes. Also, the temperatures of critical viscosities are affected by base/acid ratio and tend to decrease with an increase in base/acid ratio. These relationships were used to modify the Arrhenian and configurational entropy equations to improve the accuracy in predicting bulk slag viscosities. The modified configurational entropy approach provides more accurate predictions of viscosity of coal slags versus temperature below T_{∞} than equations based on the Urbain model or the modified Arrhenius-type equation.

7. ACKNOWLEDGMENTS

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Local Structure of a Lignitic Coal Ash Slag and Its Effect on Viscosity

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The increase of viscosity with decreasing temperature for Beulah, ND coal ash is explained by changes in the local structure of the slag resulting from the growth of microphases. The local structure of quenched slag was investigated by infrared (IR) and Mössbauer spectroscopies, differential thermal analysis (DTA), electrical resistivity, and by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The IR test was performed on samples quenched from temperatures ranging from 1100° to 1500°C. IR spectra showed seven visually resolved bands centered at 750 cm^{-1} , 870 cm^{-1} , 950 cm^{-1} , 1090 cm^{-1} , 1150 cm^{-1} , 1250 cm^{-1} , and 1350 cm^{-1} . The intense broad bands in the region of 950-1250 μm^{-1} were assigned to antisymmetric stretch vibrations of Si-O-Si and Si-O-Al modes of silica tetrahedra. The band at 1350 cm^{-1} seems to pertain to an impurity in the slag with a lower force constant than that of Si-O. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio determined by Mössbauer spectroscopy for Beulah slag is larger at 1400°C (0.96) than at 1500°C (0.88). DTA and electrical resistivity of Beulah melt indicated on rearrangements of clusters (structural units) likely resulted from the agglomeration of individual clusters.

Introduction

In recent years there has been considerable interest in predicting the viscosity of coal ash slags based on bulk ash composition.¹ Existing models, developed by Urbain² and modified by others,^{3,4} introduced several constant parameters with values dependent on the composition of the slag. The models do not allow estimation of the slag's viscosity in the region of higher viscosity. In this region many suspensions and solutions demonstrate a nonlinear relationship between shear stress and the rate of shear. Such fluids are called non-Newtonian melts. In aluminosilicate melts, the viscosity trajectory depends on the variation of their local structure with temperature. Accordingly, the main concern of our work is to provide a description

of the local structure of slag and to define major factors, other than composition, that affect the viscosity of coal ash slags.

The most important fact in establishing the glass network is the identity of the local structure. This provides information about transport properties of the slag that is helpful in predicting the slagging processes of coal ashes described by Arrhenian and configurational entropy change.⁵

The local structure of slag is described by the cluster structure (also referred to as structural unit or flow unit), its size, and connections with other clusters. These parameters directly affect the transport properties of the slag. Anionic and molecular clusters are usually identified. The anionic clusters are most often applied to describe the microstructure of the melt deduced from Raman and infrared (IR) spectra. In more complex systems, there may be more than one cluster or possibly combinations of basic clusters. Clusters may be bounded by alkali and/or alkaline-earth atoms and form agglomerates.⁶ The connection mode is given by the valence and number of alkali and/or alkaline-earth atoms adjacent to structural units.

Measurements of viscosity, density, liquidus phase relations, and thermodynamic properties provide indirect information on the silicate melt structure. To directly characterize the local structure, it is necessary to use techniques such as X-ray photoelectron spectroscopy (XPS),⁷ IR and/or Raman spectroscopies,⁸⁻¹⁰ differential thermal analysis,¹¹ high-resolution NMR spectroscopy,¹²⁻¹⁴ and Mössbauer spectroscopy.^{15,16} These investigations require the assumption that quenched melts have structural features similar to those stable at the selected soaking temperature.

Experimental Section

Measurements of Viscosity. Slag viscosity was measured in air as the temperature dropped from 1500° to 1200°C with a rotating bob viscometer described elsewhere.¹⁷ The rotating bob viscometer was a Hanke RV-2 Rotovisco unit with a 50/500 dual measuring head. Measurements were taken at 20°C intervals after stabilization of the viscosity (approximately 40 min.). The viscometer was calibrated with the National Bureau of Standards (NBS) silicate glass NBS 711. Accuracy was $\pm 5\%$.

Measurements of Melt Structure. A Nicolet 20SXB Fourier transform IR spectrometer was used to examine variations in silicate structures derived from coal ash melts. It offered high signal-to-noise ratios

and high accuracy in frequencies for spectra.¹⁶ Also, model silicate systems were employed to verify the local structure of multicomponent silicates.

Mössbauer spectroscopy was used to determine the oxidation state of iron ions in Beulah slags quenched from 1500° and 1400°C. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio was calculated as the ratio of the area of the Fe^{3+} doublet relative to the total absorption envelope. All measurements were made at room temperature.

Differential thermal analysis (DTA) and electrical conductivity tests were applied to measure the variation of slag local structure with temperature. DTA was performed using DuPont 2100 instrument in the range 1200-1440°C at a heating rate of 8 Kmin⁻¹. Electrical conductivity was measured using platinum electrodes and a Hewlett Packard Multimeter 3478A with a direct current in the temperature range of 1200°-1470°C. A Phillips x-ray diffractometer was employed to determine the crystalline phases in the slag samples.

Observation of Microstructure by SEM. Scanning electron microscopy (SEM) was employed to study the microstructure of a quenched Beulah melt. Chemical compositions from selected areas of 1-3 μm in diameter were determined by energy-dispersive x-ray analysis associated with a scanning electron microscope.

Materials. Beulah mine, North Dakota, coal ash was studied. It was prepared by burning lignite coal at 750°C for 24 hr in air. The ash was melted at 1500°C in air and homogenized by rotating bob at that temperature. The resulting slag was quenched and remelted in the Keith furnace at 1500°, 1400°, 1300°, and 1200°C; or annealed at 1100° and 1000°C, held for 0.5 hr at these temperatures, and quenched to room temperature. Three of the slags (remelted at 1500°, 1400°, and 1300°C) were quenched on a brass disc as small beads, while another set of three was quenched directly in water. The bulk composition of all quenched samples, which remained the same, is listed in Table I. Also, model glasses such as $\text{Na}_2\text{O-SiO}_2$, $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$, nepheline, and gehlenite with added iron were studied. Model glasses with compositions listed in Table I were prepared from oxides/carbonates by melting them at 1500°C, homogenizing them by rotating bob, and quenching them in water. Glass with composition similar to nepheline was melted at 1550°C and quenched in water. For IR, all samples were ground to -38 mesh before use.

Results and Discussion

Viscosity Variations with Temperature. The viscosity-temperature plot for the Beulah slag is illustrated in Figure 1. In general, viscosity increases gradually with decreasing temperature and then increases rapidly below the temperature of critical viscosity, T_{∞} . It can be assumed that the viscosity trajectory depends upon the local structure of the slag, which, in turn, depends upon the configurational entropy¹⁹ of the melt and also the dispersion of solid particles if determined below T_{∞} .²⁰ The temperature of critical viscosity has been defined as the temperature at which the viscosity of molten slag changes on cooling from those of a Newtonian fluid to those of a Bingham plastic.²¹ The Bingham plastic at rest is presumed to have a sufficiently rigid structure to resist any stress less than τ_c . When this stress is exceeded, the structure disintegrates and the material behaves like a Newtonian fluid.²² The ideal Bingham plastic fluids are suspensions. Since in ash slags and aluminosilicate melts the phase separation occurs prior to the formation of the slag's suspension, we have modified the previous definition. The temperature of critical viscosity is roughly defined as a temperature at which the composition of slag is changed from a one-phase to a two-or-more-phase mixture, and this may correspond to flow changes from Newtonian (above T_{∞}) to non-Newtonian (below T_{∞}).

IR Spectra of Beulah Glass. IR spectra provide direct information on the local structure of slags and the relationships between local structure and composition. The IR spectra for the quenched Beulah slags from 1500°, 1400°, 1300°, 1200°, 1100°, and 1000°C exhibit seven resolved bands: 750 cm^{-1} , 870 cm^{-1} , 960 cm^{-1} , 1090 cm^{-1} , 1150 cm^{-1} , 1250 cm^{-1} , and 1350 cm^{-1} (Figure 2 and Table II). The major absorption range in the spectra occurs between 900 and 1300 cm^{-1} .

Generally, vibrational frequencies are dependent on bond force constant (k), reduced atomic mass (μ), and molecular geometry; for simple diatomic T-O molecules frequencies can be estimated using classical mechanics,²³

$$\nu = (1/2\pi c) (k/\mu)^{1/2}, \quad \mu = M_1 M_2 / (M_1 + M_2) \quad (1)$$

where c is the velocity of light, M represents the mass of a T atom in the T-O diatomic molecule. The force constant may be calculated from empirical relations. For ionic crystals, k is given by²⁴

$$k = 4e^2 Z_1 Z_2 A / r^3, \quad (2)$$

where e is the electronic charge, Z is the ionic charge of atoms 1 and 2, A is the electrostatic bond strength, and r is the bond length.

Calculations using the above equations indicate that the three bands with wavenumbers 1090 cm^{-1} , 1150 cm^{-1} , and 1250 cm^{-1} behave as independent modes of the Si-O-Si(Al) network resulting from the substitution of Al for a tetrahedral Si.^{9,10} The atomic masses of Si^{4+} and Al^{3+} cations play a minor role in the frequency variation, ($\mu_{\text{Si-O}} = 10.19$, $\mu_{\text{Al-O}} = 10.04$), compared to the force constants. The ratio of force constants calculated for $k_{\text{Si-O}}/k_{\text{Al-O}}$ is ≈ 1.52 (A and r values were taken from references 25 and 26, respectively).

Day and Rindone²⁷ and Iishi et al.²⁸ have indicated that the wavenumber mode at 1250 cm^{-1} could be assigned to the vibration of Si-O-Si. McMillan et al.²⁹ have pointed out that Si-O and Al-O vibrations are strongly coupled and should move to lower frequency as the Al/Si ratio increases, due to a decrease in the effective force constant across the Al-O-Si bond (see also equations 1 and 2). Thus, aluminum can act as a perturbation on the Si-O vibration and impose new bands on IR spectra.

An important feature of polymer models for aluminosilicate melts was derived by Lawenstein.³⁰ According to Lawenstein's aluminum avoidance principle, the formation of Al-O-Al linkage in aluminosilicate is unlikely due to its inherent electrostatic instability. The aluminum avoidance principle is perfectly obeyed for melts with $\text{Si}/(\text{Si} + \text{Al}) > 0.5$.¹³ Lawenstein's principle should be maintained for the Beulah melt where $\text{Si}/(\text{Si} + \text{Al}) = 0.70$, but could be violated by gehlenite since $\text{Si}/(\text{Si} + \text{Al}) = 0.44$. Thus, on the basis of this principle, we suggest the existence of two liquid-like clusters in Beulah melt with wavenumbers at 1250 cm^{-1} and 1150 cm^{-1} that correspond to two Si-O-Si(Al) groups,

and a third cluster in gehlenite with a wavenumber of 1090 cm^{-1} that corresponds to the $=\text{Si}-(\text{O-Al})_2$ group, as shown in Figure 4.^{31,32} IR spectra of gehlenite, shown in Figure 3, match those reported in the literature in the 800 to 1100 cm^{-1} region.³³

The proposed model of clusters consists of two basic tetrahedra, SiO_4 and AlO_4 . The tetrahedral AlO_4 groups can replace SiO_4 tetrahedra in a silicate lattice in the case of a substantial excess of modifying

oxides such as alkali and alkaline-earth elements to ensure electroneutrality. This causes a change of the Si-O effective force constants. For the first cluster, the ratio of effective force constant is not changed,

$$k_{\text{Si-O}}/k_{\text{SiO}} = 1;$$

for the second cluster it is lower,

$$k_{\text{2Si-O+Al-O}}/k_{\text{Si-O}} = 0.89,$$

and for the third cluster it is the lowest,

$$k_{\text{3Si-O+2Al-O}}/k_{\text{Si-O}} = 0.77.$$

It seems likely that the configurational entropy associated with Al-O-Si links stabilizes aluminosilicate clusters. In silicates, S_{conf} is 2.99 ± 0.26 cal/mol per tetrahedrally coordinated silicon. If aluminum substitutes for silicon in the network, S_{conf} decreases to 1.98 ± 0.03 cal/mol.¹⁹

There is a continuing argument, not resolved for this manuscript, over the band at 1100 cm^{-1} . This band was also detected in sodium silicate glass with composition (30% Na_2O and 70% SiO_2) and was assigned to antisymmetric stretching of bridging oxygens within the tetrahedra.³⁴ It seems possible that both vibrations Si-O-Si and Si-O-Al of the gehlenite cluster are superimposed. The band at 1350 cm^{-1} does not appear in the spectra of SiO_2 and $\text{Na}_2\text{O-SiO}_2$ glasses (Figure 3). This band may be attributed to the presence of species in the slag other than Si-O-Si(Al), with higher reduced mass or a force constant smaller than that of Si-O diatomic molecules.

The broad band at 750 cm^{-1} is a result of the Si-O-Si symmetric stretching of bridging oxygens between tetrahedra.³⁴ The band recorded at about 870 cm^{-1} results from the presence of tetrahedral aluminum in the structure and may be assigned to the Al-O stretching vibration.³⁵ The 950 cm^{-1} band is assigned to symmetric Si-O stretching. Also, there is an apparent shift of individual bands in the quenched Beulah glass (Table II). We expect that the observed shift is caused by strongly polarizing cations^{12,36} randomly distributed in the glass and by the degree of Si, Al ordering.³⁷ Also, changes in the coordination number from XO_4 to XO_6 may cause the decrease of frequencies.²⁴ In some cases, the change in frequency because of the coordination number is not at all obvious.

The effect of iron, both Fe^{3+} and Fe^{2+} , on the IR spectra is less understood. The Fe^{3+} for Si^{4+} substitution causes a substantial shift of the Si-O-Si stretching band to lower frequencies, since the ratio of $k_{\text{Si-O}}/k_{\text{Fe-O}}$ is about 3.62 (as calculated on the basis of equation 2). The bands associated with $\text{Fe}^{3+}\text{-O}^-$ and

Fe^{3+} -O-Si lie at wavenumbers of 650-750 cm^{-1} .³⁸ Thus, the Fe^{3+} -O-Si complex may contribute to the detection of the band at about 750 cm^{-1} along with the Si-O-Si symmetric stretching of bridging oxygens between tetrahedra.

Unfortunately, the intensities of the IR bands do not grant us more details of the relative changes in the aluminosilicate complexes in these slags. The relative intensities of the bands depend on the annealing temperature. At this time we are unable to verify the factors which influence the intensity of these bands in a multicomponent system. Generally, the differences in the relative intensities of the bands are influenced by several factors, such as vibrations of a complex ion or molecule, changes of bond distance by alkali and alkaline-earth metal ions, and the T-O-T bond angle, where T = Si, Al.³⁹

Beulah Local Glass Structure Analysis by Mössbauer Spectroscopy. Iron oxide, Fe_2O_3 , may take part in the random glass network in a fashion similar to aluminum oxide. However, iron may also play the role of a modifying oxide under slightly reducing conditions and higher temperatures if its oxidation state is +2. The ratio of $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by Mössbauer spectroscopy on the 1500°C quenched slag is 0.88 and is lower than that of 0.96 recorded in the 1400°C quenched slag. This implies that below 1400°C nearly all iron exists as Fe^{3+} ions and may occupy tetrahedral positions as Al^{3+} ions do. A representative iron resonant-absorption Mössbauer spectrum is shown in Figure 5.

Local Structure of Beulah Slag above T_m and Changes in Viscosity. The IR spectroscopy tests show the likelihood that three major liquid-like clusters exist, two based on Si-O-Al connections and one based on an Si-O-Si connection. These clusters may form agglomerates when bonded by modifying cations, particularly by alkaline-earth cations during the charge balancing of Al^{3+} and Fe^{3+} ions. In alkali and alkaline earth aluminosilicates, the modifying cations are located in the vicinity of the clusters. In order to accommodate the charge balance in $[\text{Si}_2\text{AlO}_6]^{2-}$, one additional positive charge is necessary. This charge can be provided by either an alkali ion or an alkaline-earth ion. In the second place, the addition of an ion may lead to the agglomeration of clusters. Figure 6 shows examples of agglomerates likely to be formed in slags. The bond strength between clusters should depend on the cluster's structure and the z/r^2 ratio, where z is the oxidation state of a modifying cation and r ionic radii. For example, for Na^+ and Ca^{2+} , z/r^2 is 1.06 and 4.93, respectively. This implies that the bond strength between clusters and Ca^{2+} ions should be stronger than that between clusters and Na^+ ions. This is illustrated by the increase of viscosity with calcium content

in soda-lime silicates as shown in Figure 7. The base/acid ratio is the same. Thus, the increase in viscosity with decreasing temperature in the Newtonian region is assigned to the formation of agglomerates.

Additionally, the increase of viscosity in Beulah at about 1300°C may correspond to the rearrangement of Si^{4+} and Al^{3+} in clusters and the formation of gehlenite-like anionic clusters prior to crystallization. This effect may correspond to a phase separation.²⁰ It is obvious that viscosity increases in a phase-separable glass due to the change both in the composition and size of the agglomerate. The stabilization of gehlenite-like anionic clusters is referred to Fe^{3+} ions. It is known that ferric iron readily replaces aluminum in the gehlenite phase, and in Beulah slag there is about 11 wt% of iron. The vibration at 1090 cm^{-1} which suits a gehlenite anionic cluster is detected only at temperatures below 1260°C. Also, x-ray diffraction (XRD) patterns prove the existence of a gehlenite phase below 1200°C (Figure 8). This suggests that rearrangement of Al^{3+} and Si^{4+} cations in clusters during slag cooling is possible.

Most viscosity theories describe structural reorganization of the melt employing either thermodynamic or topological considerations. The viscosity-temperature relationship model is based on the consideration of the change with temperature of the configurational and vibrational entropies. Both entropies decrease with diminishing temperature, resulting in an increase in viscosity.¹⁹ The configurational entropy is defined as the entropy difference between the liquid and crystalline phases. The structural approach provides information about the network topology of melts that are characterized by gradual changes in local structure with composition. In this model, ionic motion of network-stabilizing cations is impeded due to the electrostatic forces between cations and anionic clusters which pull the cations back toward their original sites.⁴¹ This stabilizes the atomic configuration around the clusters, which, in turn, causes the viscosity to increase.⁴²

Our topological model of the agglomerate formation in Beulah coal ash slag is accompanied by a decrease of entropy with lowering temperature. This gives rise to a strengthening of the attractive forces between cations and anionic clusters in their neighborhood, and, consequently, causes the directional bonding to occur; however, some variation in bond angles is possible. They are not very strong; hence there are only small increases in viscosity. It is to be expected that the melt attains a higher density.

Another interesting problem in melt rheology is the mechanism of viscous flow in aluminosilicate melts. The mechanism is closely related to the change of oxygens between bridging and nonbridging sites:

$\text{Si-O}^{\text{w}} \rightleftharpoons \text{Si-O}^{\text{nw}}$.⁴³ An NMR study has shown that this exchange takes place at the microsecond to nanosecond time scale at liquidus temperatures, making the lifetime of silicate clusters very short.⁴⁴ This implies that the presence of agglomerates causes a small increase in the activation energy for the $\text{Si-O}^{\text{w}} \rightleftharpoons \text{Si-O}^{\text{nw}}$ exchange. The degree of increase depends on the magnitude of attractive forces between cations and anionic clusters.

The Variation of Beulah Slag Local Structure with Temperature above T_{w} as Determined by DTA and Electrical Conductivity. The DTA and electrical conductivity tests show changes in the local structure of Beulah slag in range 1200°-1470°C (Figure 9). The increase of electrical conductivity and absorption of energy at about 1360°C during heating may correspond to changes in interconnection and relative orientation of adjacent clusters. A major disorder may arise from the increased mobility of alkali and/or alkaline-earth atoms resulting from the debonding of cluster agglomerates. Generally, the increase of electrical conductivity is assigned to the increase of either ion concentration, or mobility, or both. In our system, the mobility of network modifiers is expected to occur as a consequence of the debonding of anionic clusters and modifiers. This effect is pronounced on the viscosity-temperature curve as the slow decrease of slag's viscosity (Figure 1).

Microstructure of Beulah Slag Below T_{w} Observed Under SEM. Figure 10 shows calcium-iron-aluminum silicate assemblies formed below 1200°C. Table III lists the chemical composition results determined from the three areas marked on Figure 10. Generally, all assemblies are rich in calcium, iron, aluminum, and silicon oxides. A particular microstructure observed in quenched Beulah slag can be assigned to a space-filling network with a residual, less polymerized, liquid phase rich in alkali elements trapped in the interstices.

The base/acid ratio is usually used to describe the relationship between chemical bulk composition and selected viscosity of coal ash slags. The base/acid ratio calculated for the crystallites in Figure 10 is about 0.33. This is lower than that calculated from x-ray fluorescence analysis (XRFA) chemical composition data (0.54), and significantly lower than the residual liquid phase (1.50). Thus, the viscosity of residual lightly polymerized liquid anticipated from base/acid ratio below T_{w} seems to be lower than that observed in Beulah slag determined above T_{w} . However, the total measured viscosity of slag is higher after the increase of the internal friction of the slag resulting from the formation of solid particles such as gehlenite.

Assemblies such as those noted in Figure 10 are not formed at temperatures above T_m . Generally, the alkaline-earth ions cause extensive phase separation⁴⁵ (see also Table III), so that there are in Beulah slag silica/alumina-rich regions with higher polymerization and silica/alumina-poor regions with lower polymerization.

XRD studies showed the occurrence of crystalline phases below 1200°C and confirmed the existence of crystalline phases at 1100°C. The major phase recorded on Beulah quenched from 1100°C is gehlenite and minor phases are nepheline and sodium calcium silicate.⁴⁶

The mechanisms of melt rearrangement in polymerized multicomponent aluminosilicate system can be represented as follows:

Summary and Conclusions

The viscosity of multicomponent aluminosilicate Beulah slag is significantly dependent upon its propensity for the agglomeration of anionic clusters. Agglomerates are composed with anionic clusters bounded together by modifying cations. The agglomeration process is strongly controlled by the ionic strength of alkali and alkaline earth ions. In the Newtonian region, above T_m , the agglomerates disintegrate under shear stress by breaking the weakest intercluster links. The fragmentation process causes the formation of small agglomerates and finally single clusters, which are the most mobile. Viscosity of Beulah slag depends on the size of agglomerates, and further, on the dispersion of solid phase in the slag formed below the temperature of critical viscosity.

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Table I. Composition of Starting Materials

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	Base/ Acid ^a
Beulah									
38.0	15.3	10.9	1.6	22.4	5.1	5.8	0.7	0.0	0.57
Na₂O-SiO₂									
78.2	-	-	-	-	-	21.8	-	-	0.28
Na₂O-Al₂O₃-SiO₂									
26.9	45.4	-	-	-	-	27.6	-	-	0.38
Nepheline									
42.3	30.5	-	-	-	-	27.2	-	-	0.37
Gehlenite									
33.0	29.1	8.6	0.1	29.2	-	-	-	-	0.41

$$\frac{\text{Base}}{\text{Acid}} = \frac{\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{FeO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{Fe}_2\text{O}_3}$$

Table II. Infrared Bands of Beulah Slag and Model Glasses (Summary)

Annealing Temperature (°C)	Infrared Bands (cm ⁻¹)						
	Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	Band 7
1500	749	876	965	-	1154	1252	1375
1400	755	878	960	-	1156	1250	1352
1300	749	876	9660	-	1157	1254	1352
1200	748	882	960	-	1155	1248	1347
1100	745	875	965	1085	1158	1267	1338
1000	748	874	963	1090	1147	very weak	1359
SiO ₂	760	-	-	1090	-	-	-
Na ₂ O-SiO ₂	748	-	972	-	-	1243	-
Na ₂ O-Al ₂ O ₃ -SiO ₂	757	878	975	-	-	1252	-
Nepheline	751	-	960	-	-	1243	-
Gehlenite	749	870	-	1097	-	-	-
Vibrations	Si-O-Si	Al-O	Si-O	Al-O-Si(Al)			

Table III. Composition of Assemblies and Matrix

	Analyzed Points		
	A	B	C
Na ₂ O	-	4.4	2.6
K ₂ O	3.2	2.2	5.6
MgO	-	5.0	-
CaO	29.9	48.4	16.9
SiO ₂	23.4	20.5	37.9
Al ₂ O ₃	10.9	12.8	26.3
TiO ₂	8.5	-	3.7
Fe ₂ O ₃	24.1	6.7	7.0
Acid/Base Ratio	0.49	1.50	0.33

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- Figure 1 Viscosity–temperature relationship on the Beulah slag.
- Figure 2 IR spectra of Beulah glass melt, quenched from 1500°, 1400°, 1300°, 1200°, 1100°, and 1000°C to room temperature.
- Figure 3 IR spectra of model glass: $\text{Na}_2\text{O-SiO}_2$, gehlenite, and nepheline quenched from 1200°, 1500°, and 1550°, respectively, to room temperature.
- Figure 4 Schematic representation of anionic clusters possibly formed in aluminosilicate melt of multicomponent system such as Beulah slag. The local cluster contains three structural units.
- Figure 5 ^{57}Fe resonant-absorption Mössbauer spectra of quenched Beulah melt from 1500°C to room temperature.
- Figure 6 Model of agglomerates composed of several different anionic clusters.
- Figure 7 Viscosity relations in soda-lime silicate melts.⁴⁰
- Figure 8 XRD patterns of Beulah glass quenched from 1300°, 1200°, and 1100°C to room temperature.
- Figure 9 DTA and electrical conductivity results for Beulah slag in 1200°-1470°C.
- Figure 10 Microstructure of Beulah slag quenched from 1200°C to room temperature after viscosity was measured.

Responses to Referee's Comments

Reviewer I

1. In the ninth line from the bottom of page 3, we added: "The resulting slag was quenched and remelted at 1500°, 1400°, 1300°, and 1200°C in the Keith furnace,..."
2. The discussion of "Local Structure of Beulah Slag above T_g and Changes in Viscosity" is extended on pages 8 and 9, providing the information on "How much of the viscosity change is due to agglomerate formation and how much is due to change in temperature for a Newtonian system as follows:"

Most viscosity theories describe structural reorganization of the melt, employing either thermodynamic or topological considerations. The viscosity-temperature relationship model is based on the consideration of the change with temperature of the configurational and vibrational entropies. Both entropies decrease with diminishing temperature, resulting in an increase in viscosity.¹⁹ The configurational entropy is defined as the entropy difference between the liquid and crystalline phases. The structural approach provides information about the network topology of melts that are characterized by gradual changes in local structure with composition. In this model, ionic motion of network-stabilizing cations is impeded due to the electrostatic forces between cations and anionic clusters which pull the cations back toward their original sites.⁴¹ This stabilizes the atomic configuration around the clusters, which, in turn, causes the viscosity to increase.⁴²

Our topological model of the agglomerate formation in Beulah coal ash slag is accompanied by a decrease of entropy with lowering temperature. This gives rise to a strengthening of the attractive forces between cations and anionic clusters in their neighborhood, and, consequently, causes the directional bonding to occur; however, some variation in bond angles is possible. They are not very strong; hence there are only small increases in viscosity. It is to be expected that the melt attains a higher density.

Another interesting problem in melt rheology is the mechanism of viscous flow in aluminosilicate melts. The mechanism is closely related to the exchange of oxygens between bridging and nonbridging sites. $\text{Si-O}^{\text{br}} \rightleftharpoons \text{Si-O}^{\text{nbr}}$.⁴³ An NMR study has shown that this exchange takes place at the microsecond to nanosecond time scale at liquidus temperatures, making the lifetime of silicate clusters very short.⁴⁴ This implies that the presence of agglomerates causes a small increase in the activation energy for the $\text{Si-O}^{\text{br}} \rightleftharpoons \text{Si-O}^{\text{nbr}}$ exchange. The degree of increase depends on the magnitude of attractive forces between cations and anionic clusters.

Reviewer II

1. We have verified "the effect of quenched melts on the structural features" with literature. Unfortunately, we are unable to find the reference. We believe that the reviewer is familiar with this article.
2. In the seventh line from the bottom on page 2, we added: "The rotating bob viscometer was a Haake RV-2 Rotovisco unit with a 50/500 dual measuring head."
3. In the ninth line from the top on page 3, we added: "... in the temperature range of..."
4. In the fifth line from the top on the page 4, we added: "The temperature of critical viscosity has been defined as the temperature at which the viscosity of molten slag changes on cooling from those of a Newtonian fluid to those of a Bingham plastic.²¹ The Bingham plastic at rest is presumed to have a sufficiently rigid structure to resist any stress less than τ_0 . When this stress is exceeded, the structure disintegrates and the material behaves like a Newtonian fluid.²² The ideal Bingham plastic fluids are suspensions. Since in ash slags and aluminosilicate melts the phase separation occurs prior to the formation of the slag's suspension, we have modified the previous definition. Thus, the temperature..."
5. The small difference in the viscosity of Beulah slag presented in our article resulted from the variation of ash composition.
6. The recommended article is concerned with examination of the local structure of fully polymerized glasses where a gehlenite system may be included. Since we are in the process of preparing a second article in the same area, which includes x-ray spectroscopy data, we will apply the results and discussion of Oestrike's high-resolution NMR spectroscopy data to that manuscript. We have also observed the chemical shifts of Si photopeak and splitting of 1s oxygen photopeak due to the presence of bridging and nonbridging oxygens which depends on the degree of polymerization.
7. We agree with the referee that we should introduce references, however, some of them seem to be obvious and can be found in physics textbooks, which is why we did not include them in our manuscript. Also, we wanted to limit the number of references.

Answers to Editorial Comments

1. The title on page 1 is changed from "Local Structure of a Lignite Coal Slag and Its Effect on Viscosity" to "Local Structure of a Lignitic Coal Ash Slag and Its Effect on Viscosity."
2. In the fourth line from the top on page 2, we removed "... and fouling..."
This clarifies that for this manuscript bulk transport properties are taken into account.
3. In the eighth line from the top on page 2, "The former terminology is..." is replaced by "The anionic clusters are..."
4. On page 3, "...DuPont 2100 d.t.a. instrument..." is replaced with "...DuPont 2100 instrument..."
5. On page 6, "(30/70)" is replaced by "...with composition (30% Na₂O and 70% SiO₂)..."
6. In the fourth line on page 7, we removed "...if its oxidation state is +3."
7. In the nineteenth line from the top on page 7, we added "In alkali and alkaline earth aluminosilicates the modifying cations are located in the vicinity of the clusters," and removed the sentence "Generally, [Si₃O₈]⁴⁻ ions require 6 positive charges for charge balancing."

Additional Changes Introduced in our Manuscript

1. The name of the third author is corrected to "Daniel C. Stanley."
2. A reference in Figure 6 is moved to Figure 7.
3. New References are introduced into the manuscript:
 - (21) Winegartner, E.C. In Coal fouling and slagging parameters, ASME, 1974, p 6.
 - (22) Churchill, S.W. Viscous flow. the practical use of theory, Butterworths: Boston, 1988, p 25.
 - (41) Ingram, M.D. *Mat. Chem. Phys.* 1989, 23, 51.
 - (42) Uchino, T.; Sakka, T.; Ogata, Y.; Iwasaki, M.J. *Non-Crystall. Solids*, 1992, 146, 26.
 - (43) Dingwell, D.B. *Chemical Geology* 1990, 82, 209.
 - (44) Liu, S.B.; Stebbins, J.E.; Schneider, E.; Pines, A. *Geochim. Cosmochim. Acta* 1988, 52, 527.
4. New numbers in references are introduced beginning with Reference 20.

Advanced Fuel Forms and Coproducts
Task 4.0

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EXECUTIVE SUMMARY

Significant studies on the upgrading of low-rank coals (LRCs) have been undertaken. New test methods have been developed and tested to produce advanced fuel forms, high-value added carbons and liquid coproducts. The techniques have involved cleaning, drying, aggregating, liquefying and liquid upgrading. Evaluation of dried coal products as advanced fuel forms included testing for physical stability towards moisture reabsorption and dust generation. Acid cleaning and fine-coal aggregation via oil agglomeration have been investigated along with an economic assessment of chemical cleaning of LRCs. Testing of the activated char product included sorption of SO_2 at ambient and elevated temperatures. Novel heterogeneous catalysts for upgrading first-stage coal liquefaction products were also tested. A brief outline of a supported visit to the Asia-Pacific Economic Cooperation (APEC) Energy Experts' Group Technical Seminar on Clean Coal Technology in Thailand is presented. Summaries of the different sections of this task are given below.

Dust Generation

Low-sulfur subbituminous coals have high moisture content and consequently low heating value, leading to boiler derating in U.S. midwestern and eastern utilities as well as switching and/or blending coals to achieve SO_2 compliance. In their drive to develop cost-effective coal-drying processes, the coal developers have focused on heat content of the products and neglected the critical stability issues of friability and dusting, moisture reabsorption and spontaneous heating. The Energy & Environmental Research Center (EERC), in an effort to establish new standards for dried products, has used various known methods as well as developed new methods to evaluate the propensity of lump western coals, raw and dried, to produce dust and absorb water. Three drying methods—air, hot-water, and saturated-steam—were used to generate low-moisture upgraded products. New indices for dust generation and friability were determined for assessing the effect of moisture removal and upgrading methodology on coal stability. Analysis of the dried coals using various strength tests indicated that the reduction in moisture made the lump coal unstable, yielding substantially higher dust and friability indices relative to those of the raw coals. Moisture reabsorption tests showed that air-dried products regained moisture, while hydrothermally dried products resisted moisture absorption.

Oil Agglomeration

Tar oil, a coal gasification product, was identified as suitable for low-shear agglomeration of LRCs. In contrast, tar oil lights, the distilled fraction of tar oil, were ineffective for agglomeration at low shear due to oil polymerization. However, tar oil lights dissolved in a polar material (ethanol or crude phenol) along with high-shear mixing induced agglomeration. While tar oil lights appeared to enhance the integrity of air-dried agglomerates, heating the agglomerates to reduce the oil to 5% or less reduced their strength for lump fuel handling, but their equilibrium moisture content (5 wt%) was comparable to that for bituminous steam coals and showed virtually no tendency for moisture reabsorption. Some 99 wt% of the remaining oil in the process water was removed by adsorption onto coal.

Two process modifications for inorganic reduction of LRCs were investigated: carbonic acid treatment for organically associated elements and selective agglomeration for minerals. Carbonic acid treatment at 85 psig removed between 63 and 80 wt% of the total sodium in several lignite and subbituminous coals. Selective agglomeration testing of a high-ash subbituminous coal achieved 90 wt% coal recovery and over 35 wt% ash reduction but no reduction in total sulfur. The EERC agglomeration process, without chemical cleaning or pH adjustment of the process water, successfully agglomerated several LRCs. However, magnitude economics assessment showed that chemical cleaning is cost prohibitive if included in a commercial oil agglomeration plant for producing a switching or blending fuel for the steam coal market. The potential for producing a high heating value oil rests on identifying a suitable agglomerating oil for about \$10/ton.

APEC Energy Experts' Group Technical Seminar in Thailand

The EERC was requested by U.S. DOE to participate in the Technical Seminar on Clean Coal Technology in Chiang Mai and Bangkok, September 6-10, 1993. This seminar was held in response to the growing public, private, and government concerns relating to the increased use of lignite for power generation in Thailand. The EERC paper, "Upgrading of Low-Rank Coals for Conventional and Advanced Combustion Systems," coauthored by B.C. Young (presenter), M.A. Musich, and M.L. Jones, one of 25, was well-received by the 60 delegates from 13 countries at Chiang Mai. Summaries of the four session areas discussed at the Technical Seminar were presented at the public seminar attended by approximately 170 people in Bangkok. Questions on energy and environmental issues invited from the audience were fielded to selected panel members and other delegates who attended the Technical Seminar. The proceedings of the Technical Seminar were published by the East-West Center, Honolulu, HI in December 1993.

Coproducts

Two projects fell within the coproducts subtask: upgrading chars and upgrading primary liquids from the pyrolysis of selected low-rank coals to meet marketplace product specifications. The high reactivity of LRCs is assumed to give them an advantage in developing high surface area activated carbons.

The SO₂ sorption capacity of steam-activated chars made from Alaskan Beluga subbituminous coal and North Dakota lignite and leonardite coals was determined at elevated temperatures (100°C). Leonardite char produced under rapid heatup conditions at 750°C exhibited the highest SO₂ adsorption, greater than that of tested commercial coal-based chars. Since pyrolysis of lignite leads to decrepitation, pelletizing the lignite char particles with a polyvinyl alcohol binder improved the product stability towards handling and moisture without adversely affecting the sorption capacity.

Exploratory techniques were investigated for preventing polymerization reactions of volatile species and for controlling cracking of lighter products in the liquids and gases from the pyrolysis of leonardite in a modified fluidized-bed reactor. Tests using infrared spectrometry and open-column chromatography on the aromatic and polar tars from the char produced in the presence of a specially prepared hydrotreated NiSMM (nickel-substituted micra montmorillonite) catalyst revealed 90% aromatic and polar material. This catalyst also reduced carbon monoxide levels and increased levels of methane under

elevated pressure conditions at 600°–630°C compared to those levels when no catalyst or a catalyst not hydrotreated was used. Additional work is planned to complete this part of the project.

Low-Rank Coal Liquefaction

Coal can be effectively solubilized by treatment with carbon monoxide reductant in aqueous solvent as in the CO steam process. Sodium aluminate has been demonstrated to improve the conversions to soluble intermediates in the CO/H₂O system and in water–hydrogen donor solvent mixtures. The importance of this effect in the subsequent catalytic depolymerization of the solubilized intermediates was examined. The catalytic hydrotreatment of the solubilized low-severity products from sodium aluminate-catalyzed and from uncatalyzed CO/H₂O reactions of a Wyodak subbituminous coal were compared using three catalytic reactions as well as a thermal noncatalytic reaction.

Catalytic hydrogenations of the THF-soluble fractions obtained from the two low-severity products were performed with a conventional cobalt–molybdenum catalyst as well as with two clay-supported iron catalysts at 425°C for 3 hours in the presence of 1000 psi (cold) H₂. The sodium aluminate had little effect with respect to the total liquefaction conversion to oils when the efficient cobalt–molybdenum catalyst was used for the hydrotreatment step. However, the two clay-supported iron catalysts yielded significantly different conversions of THF-soluble intermediates from the sodium aluminate-catalyzed and from the uncatalyzed reactions to heptane-soluble oils. These catalysts gave 68% and 62% conversions to heptane solubles from the sodium aluminate-catalyzed low-severity product and 56% and 47% conversions from the uncatalyzed low-severity product. The thermal reaction gave poor conversion to heptane solubles for both low-severity products.

These results have important implications for multistage liquefaction processing schemes. The very effective hydrogen-activating molybdenum sulfide catalyst can compensate for the lower quality of the uncatalyzed low-severity reaction product. Further, in the event of utilizing inexpensive and disposable iron catalysts, the use of sodium aluminate in a pretreatment solubilization step will be critical to increasing the yields obtained in the subsequent catalytic hydrogenation step.

Addition of iron salts plus sodium aluminate in the CO/H₂O solubilization step has been demonstrated to improve conversion. Recent studies on the mechanism of iron aluminate catalysis of liquefaction in hydrogen-donor solvents show that carbon monoxide acts more like a water–gas shift reactant. Work with model compounds demonstrates that CO is required to activate the iron aluminate for catalytic hydrogen-transfer reactions between solvent and coal. The activation effect is much more important in hydrogen transfer involving polynuclear aromatics.

TASK 4.0 ADVANCED FUEL FORMS AND COPRODUCTS

Subtask 4.1 Beneficiation for Advanced Systems

Dust Generation

INTRODUCTION

The Energy & Environmental Research Center (EERC) has participated in the assessment and development of a variety of low-rank coal-drying technologies. Current with the development of these drying technologies, the EERC has commenced a systematic program to investigate the major stability issues of dried low-rank coals (LRCs).

The work presented in this report describes the preliminary results of the development of laboratory tests to assess the stability of low-rank coals treated by conventional- and advanced-drying/pyrolysis processes. Because stability phenomena are often given only minor attention, the development of improved stability-testing methods was deemed a necessary yet complimentary component in the successful demonstration of upgrading technologies (1).

Three drying methods (air, hot-water, and saturated-steam) were used to generate low-moisture, upgraded products for physical stability measurements. Standard test methods as well as methods developed at the EERC were used to evaluate the propensity of lump western LRCs (raw and dried) to produce dust and absorbed water. Indices for dust generation and friability were generated for raw and upgraded coals to observe the effect of moisture removal and upgrading methodology on coal stability. Spontaneous combustion testing or "self-heating" studies on LRC and dried LRCs are planned to begin in 1994.

Background

LRCs represent nearly half of the estimated coal resources in the world. In many developing nations they are the only source of low-cost energy. Relative to bituminous coals, low-rank coals are less costly to mine, generally have lower sulfur and ash contents, and are more reactive; LRCs, however, have higher moisture contents and lower heating values.

Low-rank coal utilization has largely been restricted to power generation at or within short haulage from the mine because of the high moisture content and low heating value of this coal type. Continuing a trend of the last decade, bituminous-fired utilities in the midwestern and eastern U.S. are investigating low-sulfur subbituminous coals for switching and/or blending to achieve compliance SO₂ emissions. In many instances the low heating value of the subbituminous coals results in intolerable boiler derating. Consequently, the driving force exists for coal producers to develop cost-effective coal-drying processes to enhance LRC heating value and reduce transportation costs.

The LRC upgrading technologies currently demonstrated include evaporative and nonevaporative drying and mild pyrolysis/gasification. An obstacle facing their development is the stability of the product toward dusting, moisture reabsorption, and

spontaneous combustion. Unfortunately, upgrading may enhance the instability towards at least one of the above criteria. Currently, four ASTM procedures are available to address the physical stability of coal or coal-derived products: D1412-86 (equilibrium moisture), D441-45 (tumbler test), D409-71 (Hardgrove index), and D440-49 (drop-shatter test) (2). To date, an accepted procedure for the determination of dust index (previously D547-41) does not exist and the suitability of the equilibrium-moisture procedure for raw and upgraded LRCs has been questioned.

Experimental Procedure

Coal Preparation and Drying

Coals processed in subsequent drying tests were sized to 12.7 x 6.7 mm via stage crushing and bottom sizing. This size range was determined to be representative of upgraded coals produced by drying and pyrolysis processes currently in stages of development ranging from bench- through demonstration-scale (3,4).

The three coal-drying methodologies tested included air drying, hot-water drying (HWD), and saturated-steam drying (SSD). Air drying was performed to observe the effects of low-temperature, evaporative drying on coal stability. In this process, the sized coal was air-dried, uncovered, in a laboratory hood at the prevailing temperature and humidity. After an initial drying period of approximately 24 hours, the coal mass was determined and the coal-moisture content calculated, assuming weight loss was due to moisture evaporation only. The drying period was extended, as necessary, until the desired, calculated, moisture content was attained; the total coal-moisture content was verified by ASTM Method D 3173. The samples were then double-bagged to prevent oxidation and moisture reabsorption.

The hydrothermal drying processes, hot-water drying and saturated-steam drying, were performed to observe the effects of nonevaporative drying on coal stability. During HWD the coal is totally immersed in the water phase, whereas during SSD the coal is in contact with only the vapor phase (saturated steam). The hydrothermal drying processes operate at or above the saturated-steam pressure associated with the specific temperature of processing. At saturation conditions water is removed from the coal as a liquid rather than vapor. The removal of coal moisture via hydrothermal treatment is hypothesized to be caused by a collapse of the coal pore structure, differential expansion of water relative to the coal matrix, and pneumatic displacement by CO₂ (the product of decarboxylation). The collapse of the pore structure, the plugging of micropores and the coating of surfaces by tar, and reduction of hydrophilic sites (carboxyl and carbonyl groups) allow the treated product to resist significant moisture reabsorption.

The systems and procedures for hydrothermal treatment have been described elsewhere (4-6). Briefly, hydrothermal drying tests were performed in an externally heated 2-gallon autoclave equipped for temperature measurement/control and pressure measurement. HWD was performed on slurries containing approximately a 1:1 sized coal-to-deionized water ratio; SSD tests were similarly performed, except the coal-to-water ratio was 4:1. Typically, 2000 grams of coal were treated at 300°C for 30 minutes whereafter the autoclave and contents were allowed to cool overnight prior to recovering the treated coal and process water. The masses of raw and treated coal and feed and process water and the volume of process gas were measured to determine material balances.

Durability Testing

A modified-ASTM tumbler test was used to determine the relative friability and abrasiveness of the sized, raw, and treated coals during simulated handling. The main internal flights were adjusted to accommodate a smaller coal size, 12.7 x 6.7 mm. The dimensions of the tumbling apparatus, with lifting shelf inserts, are presented in Figure 4.1-1. The test program examined the effect of varying the shelf dimensions on the repeatability of friability and dust indices. The gap between the ledge and the edge of the tumbler cell was varied from 15.9 mm ($5/8$ "") to approximately 3.18 mm ($1/8$ "").

Prior to tumbler testing, the weights of test coals retained on 9.5-mm and 6.7-mm screens were determined. These two screen fractions were recombined prior to tumbler testing. Tumbler tests were performed by varying rotational speed (40 to 80 rpm; ASTM = 40 rpm), coal charge (100 to 1000 grams; ASTM = 1000 grams), and total revolutions (600 to 14,400; ASTM = 2,400). Tumbled coal samples were classified into seven size-fractions ranging from 9.5 mm to 0.60 mm. The weights of the feed and tumbled coal-weight fractions were used to calculate the tumble index (T_i), defined by [Eq. 4.1-1], for each screen size-fraction.

$$T_i = (W_T - W_F) \times (100/W_A) \quad [\text{Eq. 4.1-1}]$$

where W_T = Weight of tumbled coal for screen size i, grams
 W_F = Weight of feed coal for screen size i, grams
 W_A = Weight of total feed coal for tumbler test, grams

Figure 4.1-1. ASTM- versus modified-tumbler cell design.

This equation was derived to remove the effect of feed-coal-size and sample-mass variations on tumbler results thus allowing comparison of different coal types.

In addition to tumble indices, the screening results from durability testing were converted to friability and dust indices. Background on the ASTM tumbler tests and calculation of friability indices are presented elsewhere (2). The "s" factor was calculated using [Eq. 4.1-2], and the friability indices were calculated by [Eq. 4.1-3]. The former equation represents a modified method of calculating the "s" factor, which relates the fraction of coal on individual screens to the average feed-coal size rather than that of the top screen only (ASTM procedure). Reference to an estimated average particle size for the feed coal broadens the base point used for calculations, thus more accurately reflecting the variability and size of the feed coal. The sample's dust indices were determined similarly to ASTM procedures by simply measuring the weight percent of coal passing the 0.3 mm (50-mesh) screen.

$$s = \text{wt}\%_{(\text{on screen})} \times A_{is}/A_p \quad [\text{Eq. 4.1-2}]$$

where A_{is} = Average initial screen size
 A_p = Estimated average particle size of feed material

$$\text{Friability } (\%) = 100 - \Sigma s \quad [\text{Eq. 4.1-3}]$$

A modified ASTM D440 drop-shatter test was also used to determine the relative size stability and its complement, friability, via a method similar to the tumbler test. Drop-shatter testing is used to estimate the ability of coal to withstand breakage when subjected to handling at the mine and during transit to the consumer. In this test, 50 grams (50 lb, i.e. 2268 gram, in ASTM method) of raw or dried coal was classified to determine size distribution, recombined, and then dropped through a 1.83-m section of PVC pipe. Each coal sample was dropped ten consecutive times, and classification was performed after the second, sixth and tenth (final) drop.

Coal durability testing was also completed on Colstrip samples using a modified Jameson cell, developed at the University of Newcastle (Australia). The Jameson unit consists of ASTM tumbler cell with an in-line dust-collection system. This test method combines the tumbler and dust tests into one procedure. Results are determined by sieve analysis, amount of dust collected, and the moisture content of periodic samples.

Dust Testing

Prior to 1986, the labor-intensive ASTM dusting-index test (D547-41), was used to measure respiratory and explosive dust occurring from the handling of coal. This procedure, which required large samples of coal, is no longer accepted due to large experimental errors (20% or more). Recent efforts focused on standardizing a new method that incorporates better dust-analyzing equipment and continuous data logging to reduce experimental error (7).

To simulate the dustiness test, a light-scattering device was attached to a 59.5-dm³, cylindrical vessel with a height of 1.3 m. The vessel was equipped with a top seal and a sample-dumping section through which approximately 100 grams of raw or treated coal was introduced. After dropping the sample into the drum, the seal was quickly

positioned. Dust-laden air was withdrawn through one of two sample ports located along the drum wall at 0.61 m and 0.91 m above the drum base. The air was drawn through a real-time aerosol monitor (RAM-1) that measured the concentration of airborne particulates less than 20 microns in size. Data were collected over 10-minute increments or until the particulate concentration returned to zero.

Moisture Reabsorption

Modifications to the ASTM D1412 equilibrium-moisture procedure were investigated to observe dependence on particle size, sample preparation, and incubation period. All equilibrium-moisture tests were performed under vacuum at 30°C and 96% to 97% relative humidity. The test-chamber humidity was maintained by a saturated potassium sulfate (K_2SO_4) solution. The equilibrium moisture for each coal type was presented as the average of three determinations.

The applicability of the 3-day incubation period (ASTM D-1412, suggested for LRCs and coal products) was evaluated by two, modified, equilibrium-moisture procedures. Coals were sized to the ASTM-specified -1.2 mm(-16 mesh) prior to testing. The first modified equilibrium-moisture test investigated the attainment of constant sample weight as the indicator of equilibrium. Modified procedure #1 included measurement of the initial moisture content of the sample. The weight-loss measurements were used to calculate moisture contents by [Eq. 4.1-4], assuming that weight loss was due entirely to moisture evaporation. The incubation period was extended until the calculated moisture contents did not change by more than a net 0.5% over a 24-hour period. Upon completion of testing, the calculated equilibrium-moisture content, M_e (wt%), was compared to the ASTM-moisture content measured by weight loss at 105°C.

$$M_e = 1 - (W_i [1 - M_o] / W_o) \times 100 \quad [\text{Eq. 4.1-4}]$$

where W_i = Sample weight on day i , grams
 W_o = Initial sample weight, grams
 M_o = Initial moisture content, wt%

A second modified equilibrium-moisture procedure was also investigated. Modified Procedure #2 entailed an extended incubation period and its effect on equilibrium moisture. An average initial moisture content was determined with two subsamples, and the remaining eight subsamples were incubated. Two samples were removed for determination of instantaneous moisture content after incubation periods of 3, 5, 7, and 10 days, thus exhausting the supply of samples on the tenth day. Calculated moisture contents were determined via [Eq. 4.1-4]. The moisture content after 3 days of incubation (ASTM specification) was compared against moisture contents determined on subsequent days.

The effect of preincubation sample-preparation methods on the final- or equilibrium-moisture of raw or treated coals was evaluated by comparing the results for wetted samples (ASTM procedure) and surface-dry samples. The samples, sized to 12.7 x 6.7 mm, were incubated for three days after which the moisture content was determined. Similarly, the effect of sample particle size on the final or equilibrium moisture of raw or treated coals was evaluated by comparing the results for lump-coal samples and -1.2-mm samples.

Results

Drying Testing

Hydrothermal-drying tests were performed with three coals, Knife River lignite (North Dakota), Colstrip subbituminous (Montana), and Little Tonzona Creek subbituminous (Alaska). Saturated-steam drying and hot-water drying were performed at 300°C. Table 4.1-1 summarizes the proximate and ultimate analysis (equilibrium-moisture basis) for raw and dried coals. The changes in each coal caused by the drying processes included irreversible removal of moisture, enhancement of heating value, and reduction of oxygen content (via decarboxylation). The theoretical emissions of ash and SO₂ (lb/MMBtu) were: 1) significantly reduced for the Colstrip subbituminous; 2) significantly increased for the Knife River lignite; and 3) relatively unchanged for the Little Tonzona subbituminous. The sodium and potassium contents of the HWD coals were substantially reduced; similar reductions were not observed with SSD coals (8).

The product recoveries, summarized in Table 4.1-2 for each test, ranged from 84 to 97 wt%, although Btu recoveries were proportionally higher because of the enhancement of heating value. The particle-size reduction due to hydrothermal processing was determined by comparing average particle-size distributions, as determined by dry classification, of the feed and dried coals. These results indicated that more breakage or shrinkage occurred to the subbituminous coals than to the lignite coal.

Each test coal was weighed and classified before and after hydrothermal treatment. Coal-size reduction results, presented in Table 4.1-2, are also summarized in terms of friability and dust indices in Table 4.1-3.

Durability Testing

Prior to evaluation of dried coals, tumbler tests were performed with sized, raw Colstrip and Little Tonzona subbituminous coals to determine appropriate tumbling parameters: lifting shelf dimensions, mass of coal sample, tumbler speed, and total revolutions. Tests were first performed using two different lifting shelves, as shown in Figure 4.1-1; an ASTM-specification tumbling speed of 40 rpm and total revolutions of 2400 were used in each test. Friability and dust indices of raw coals tumbled with the ASTM-specification lifting shelf (1.6-cm gap; 1.9-cm ledge) were 30% to 50% lower than indices obtained when tumbling the same coals with the modified lifting shelf. Tumbler testing also indicated a substantial increase in fines production as the revolutions increased, little difference in fines production as tumbler speed changed, and a proportional relationship between fines generated and the amount of coal used for the tumbler test (8). However, the repeatability of indices was adversely affected by a reduction in coal test quantity (100 grams versus 1000 grams) when using the ASTM-specification lifting shelf. Because of the limited amount of dried coals available for subsequent testing, the modified lifting shelf was considered necessary to assure sufficient test-coal agitation and yet to achieve repeatability of indices.

Further, an evaluation of tumbling speed was performed on the raw, sized coals by comparing friability and dust indices obtained at 40 rpm and 2400 revolutions (ASTM specifications) and 80 rpm and 2400 revolutions. The indices were not substantially

TABLE 4.1-1

Proximate, Ultimate, and Heating Value for
Raw, HWD¹, and SSD² Subbituminous and Lignite Coal (Equilibrium-Moisture Basis)

Coal Type:	Little Tonzona			Colstrip			Knife River		
Drying Type	—	HWD	SSD	—	HWD	SSD	—	HWD	SSD
Equil. Moisture, wt%	31.0	11.1	9.5	25.3	9.3	8.6	35.1	15.0	12.6
Proximate, wt%									
Volatile Matter	36.1	39.4	39.1	29.9	34.4	34.2	29.7	35.1	36.2
Fixed Carbon	25.8	39.5	41.0	37.2	47.6	48.2	27.7	38.8	39.9
Ash	7.1	10.0	10.4	7.6	8.7	9.0	7.5	11.1	11.3
Ultimate, wt%									
Hydrogen	6.8	5.2	5.1	6.0	5.3	4.9	6.7	5.4	5.3
Carbon	41.2	58.3	59.1	50.4	63.8	63.8	40.3	55.7	56.9
Nitrogen	0.5	0.6	0.6	0.5	0.7	1.0	0.5	0.7	0.8
Sulfur	1.1	1.3	1.2	0.8	0.8	0.7	0.9	1.4	1.4
Oxygen	43.4	24.6	23.5	34.7	20.6	20.6	44.0	25.7	24.3
Ash	7.1	10.0	10.4	7.6	8.8	9.0	7.5	11.1	11.3
Heating Value, Btu/lb	7,030	10,030	10,200	8,550	10,850	10,830	6,740	9,400	9,550

¹ HWD, hot-water-dried.² SSD, saturated-steam-dried.

TABLE 4.1-2

Material Balances, Btu Recovery, and Moisture-Reduction
Summary for 300°C-Hydrothermal-Drying Tests

Coal Type:	Little Tonzona		Knife River		Colstrip	
Drying Type	HWD	SSD	HWD	SSD	HWD	SSD
Solids Recovery, wt%	84.6	83.6	96.6	90.4	94.3	93.2
Btu Recovery, %	93.8	92.5	102.8	95.2	98.5	96.5
Particle-Size Reduction, %	12.6	9.8	7.2	4.5	10.8	17.6
Moisture Reduction, wt%	62.6	68.0	62.5	64.5	57.3	64.1

TABLE 4.1-3

Hardgrove Index, Friabilities, and Dust Indices for
Raw, AD¹, HWD, and SSD Subbituminous and Lignite Coals

Coal Type:	Little Tonzona				Colstrip				Knife River			
Type	Raw	AD	HWD	SSD	Raw	AD	HWD	SSD	Raw	AD	HWD	SSD
Moisture, wt%	30.0	9.0	8.5	7.2	22.5	10.7	9.4	4.4	37.5	8.1	9.6	11.6
Hardgrove Index	21	ND ²	69	64	44	ND	65	64	64	ND	74	74
Processing												
Friability, %	ND	ND	13.4	14.3	ND	ND	7.1	4.6	ND	ND	10.9	17.6
Dust Index, %	ND	ND	0.7	0.4	ND	ND	0.6	0.2	ND	ND	1.1	0.4
Tumbler Test (2400 revolutions)												
Friability, %	6.7	14.1	20.9	37.1	7.2	26.0	33.0	39.2	7.2	37.4	41.1	38.4
Dust Index, %	0.7	2.9	6.8	13.6	1.7	7.0	6.2	10.3	1.7	6.0	10.3	7.5
Drop-Shatter Test (10 Drops)												
Friability, %	3.8	13.2	20.7	26.6	10.7	33.1	26.3	40.5	5.3	35.6	34.8	34.2

¹ AD, air dried.

² ND, not determined.

different; consequently the higher tumbling speed (80 rpm) was implemented to test dried coals and to allow testing of more coal samples within the study test period.

The appropriate insert dimensions and tumbling speed were established prior to performing tests on sized raw, air-dried (AD), HWD, and SSD samples of Colstrip and Little Tonzona subbituminous coals and Knife River lignite. Revolutions were varied from 1200 to 14,400 in 1200 increments. As an example, Figure 4.1-2 illustrates the effects of varying the total revolutions for 100-gram samples of raw, AD, HWD, and SSD Colstrip coals. A negative tumble index reflects a net mass reduction for a particular coal size as a result of comminution; conversely, a positive tumble index reflects a net mass increase for a particular coal size due to comminution of larger particles. The moisture content of the tumbled samples, and the method of drying may both have been factors affecting the level of coal comminution. The AD, HWD, and SSD Colstrip coals, with tumbler-tested moisture contents of 10.7, 9.4 and 4.4 wt%, respectively, experienced significant reduction of the +6.7-mm fractions relative to the raw coal that was tested at 30 wt% moisture. In addition to tumble index, the friability and dust indices were also calculated and are summarized in Table 4.1-3 for the three different coal samples. Results reported in Table 4.1-3 represent 100-gram tests performed at 80 rpm for 2400 revolutions. Table 4.1-4 summarizes the sieve analysis, estimated average particle size, and indices for tumbling tests completed with Colstrip coal samples.

Drop-shatter test results for two- to ten-drop tests on the raw coals indicated that Little Tonzona friability index varied from 0.7 to 3.8, while the more friable Colstrip and Knife River coals varied from 2.0 to 10.7 and from 0.5 to 5.3, for two to ten drops, respectively. The friability indices of all dried coals were significantly higher than those of the parent coals, reemphasizing that dried samples are anticipated to be much more susceptible to excessive breakage when handled. Results for the drop-shatter test program are summarized for ten-drop data and presented in Table 4.1-3.

Figure 4.1-2 Tumble indices for raw, AD, HWD, and SSD Colstrip as a function of total revolutions

TABLE 4.1-4

Summary Information from Tumbler Tests Conducted on Various Colstrip Samples

Type	Raw		Air-Dried		HWD		SSD	
Moisture, wt%	22.5		10.7		9.4		4.4	
Revolutions	—	2400	—	2400	—	2400	—	2400
Ave. size, mm	10.5	9.5	10.0	7.0	9.7	6.5	9.3	5.7
Size, mm	Cumulative Weight Percent Retained on Screen							
9.5	81.1	58.1	63.6	20.8	54.0	11.2	40.1	8.2
6.68	100.0	90.0	100.0	59.2	100.0	53.8	100.0	45.3
4.75	100.0	95.5	100.0	74.6	100.0	71.7	100.0	61.2
2.36	100.0	97.3	100.0	86.3	100.0	83.8	100.0	73.0
1.18	100.0	97.7	100.0	90.1	100.0	88.3	100.0	80.7
0.03	100.0	98.3	100.0	93.0	100.0	93.8	100.0	89.7
Friability Index %	9.8		26.0		33.0		39.2	
Dust Index %	1.7		7.0		6.2		10.3	

Table 4.1-3 also presents the test moisture of the coal samples and the Hardgrove indices in the various samples. Similarities were realized in ten-drop and tumbler friability data. However, substantially more fines were generated during tumbler tests for the same three Colstrip samples. This indicates that the tumbler test had more attrition, and drop-shatter testing presented more of an impact test to the coal product.

Figures 4.1-3 and 4.1-4 summarize the results from Jameson test results for raw and treated Colstrip samples when tumbled in the ASTM cell for 180 minutes. Figure 4.1-3 indicates a dramatic decrease in raw-coal-moisture content to 9 wt%, while only slight variances in moisture content for the treated samples. Figure 4.1-4 represents the amount of fines, classified as -0.8-mm material, versus tumbling time for the same three Colstrip samples. This figure indicates that fines amounts increase substantially for the raw coal as the coal dries, similarly to that in the treated products. These results indicate that for the three drying methods evaluated, the amounts of fines that were generated were not necessarily process-specific but more closely relate to the moisture content of the individual fuel.

Figure 4.1-3 Jameson test results, moisture content versus tumbling time, for various Colstrip samples.

Figure 4.1-4 Jameson test results, amount of fines versus tumbling time, for various Colstrip samples.

Dust Testing

Dust-testing results are reported in Table 4.1-5, including the maximum and average concentrations and the total amount of dust collected during data logging. The results indicated a substantial increase in dust generation between raw and dried coals for all three test coals. In addition, as with all of the other stability tests, as the moisture decreased, the amount of fugitive or nuisance dust (20 microns and below) increased. Trends similar to those of the other stability tests were found for the raw coals; namely, Little Tonzona generated the least amount of dust, followed by Knife River and Colstrip. Also, Table 4.1-5 illustrates the large increase in dust generation of samples that have been tumbled as compared to coal samples that were not tumbled. This increase may be partially attributed to a decrease in moisture (approximately 1 to 2 wt%) as the coal was tumbled.

Moisture Reabsorption Testing

Equilibrium-moisture determination tests, using ASTM and modified procedures, were performed on raw, AD, HWD, and SSD samples of Colstrip and Little Tonzona Creek

TABLE 4.1-5

Dust Generation by Raw, HWD, and SSD Coal Samples

Fuel Type	Moisture, wt%	Tumbled, yes/no	Maximum, mg/m ³	Average, mg/m ³	Total, µg
Little Tonzona					
Raw	30.0	no	2.2	1.1	22.9
Raw	27.5	yes	18.7	8.5	171.1
HWD	8.5	no	5.6	2.3	46.6
HWD	7.5	yes	32.4	10.2	205.4
SSD	6.0	no	11.5	5.0	101.1
SSD	5.0	yes	36.6	12.2	245.7
Colstrip					
Raw	22.5	no	2.7	1.2	24.2
Raw	21.2	yes	16.2	6.6	132.2
HWD	9.4	no	2.6	1.7	34.2
HWD	7.2	yes	22.6	10.2	206.2
SSD	4.8	no	6.1	2.6	51.6
SSD	3.0	yes	20.7	12.5	252.6
Knife River					
Raw	37.5	no	2.8	1.2	23.4
Raw	35.5	yes	39.8	17.1	345.3
HWD	9.6	no	13.1	4.0	81.7
HWD	7.0	yes	100.1	21.0	424.5
SSD	11.6	no	8.6	2.6	53.3
SSD	9.7	yes	53.5	18.1	365.0

subbituminous coals and on the Knife River lignite. The moisture contents of the coals (-60 mesh) attained after three days of incubation (ASTM specifications) are presented in Table 4.1-6. Notable results were significant reductions in moisture-holding capacity for all three coals; saturated-steam drying had a somewhat greater effect on reducing the moisture reabsorption capabilities of the subbituminous coals relative to air drying and HWD. Air drying apparently caused coal changes, possibly pore collapse, sufficient to prevent moisture reabsorption to the levels of the raw coals.

Equilibrium-moisture values obtained by extending the incubation period until relatively constant coal sample weight was attained (modified Procedure #1) are also presented in Table 4.1-6. Incubation periods ranged from 6 days (for SSD Little Tonzona) up to 18 days (for raw Knife River). Weight losses between the third and fourth days of incubation were, in many instances, significant since the calculated moisture contents (determined by [Eq 4.1-4]) were up to 4% lower after one additional day of incubation. However, the equilibrium-moisture content did not necessarily appear to be related to the weight loss of the sample during incubation. For example, raw and dried Colstrip samples had essentially identical equilibrium-moisture contents after the standard three-day period and after extended periods that ranged up to 13 days total. But over the extended periods the samples lost an additional 15-20 wt% in mass. This result seems to contradict the assumption of weight loss via moisture evaporation only.

TABLE 4.1-6

Equilibrium-Moisture Content Results

Fuel Type	ASTM (1.18 mm x 0)		12.7 x 6.7-mm (No Size Reduction)	
	3-Day	Extended ¹	Saturated	Unsaturated
Knife River				
Raw	37.1	35.1	38.5	35.1
Air Dried	32.3	28.2	33.8	24.3
Hot-Water Dried	19.4	15.0	12.8	11.9
Steam Dried	14.3	12.6	14.8	14.4
Colstrip				
Raw	25.7	25.3	25.7	25.3
Air Dried	20.7	20.6	23.6	21.5
Hot-Water Dried	9.6	9.3	10.0	10.7
Steam Dried	8.4	8.6	7.3	7.0
Little Tonzona				
Raw	34.0	31.0	30.4	30.6
Air Dried	30.4	26.4	30.2	25.1
Hot-Water Dried	22.8	11.1	10.8	10.4
Steam Dried	18.4	9.5	9.4	8.7

¹ Modified Procedure # 1.

With the Little Tonzona coals, the extended incubation periods most notably influenced the equilibrium-moisture contents of the SSD and HWD coals. This may be explained by an unusually high surface-tar concentration that effectively reduced the micropore volume available for holding moisture. Overall the results indicated that a three-day incubation period may be unsuitable for some forms of LRCs, and associating the attainment of constant weight with true equilibrium moisture may not be valid.

Extended equilibrium-moisture tests using modified Procedure #2 were performed with raw and HWD Colstrip subbituminous coals. Moisture contents measured on the tenth incubation day were approximately 2% lower than the moisture content determined after the ASTM-specified 3 days. A larger deviation was observed with the AD Colstrip sample in that the moisture content on the tenth day was 6% lower than the value obtained on the third day. Preliminary results using modified Procedure #2 indicate that 5-, and more likely, 7-day incubation periods may be more applicable for determination of equilibrium-moisture contents of raw and dried LRCs. The calculated equilibrium-moisture values were in reasonable agreement with the measured values and typically did not differ by more than 0.5% in net value.

The results of preliminary tests, to observe the effect of sample preparation on equilibrium-moisture values, are also presented in Table 4.1-6. The raw, HWD, and SSD samples of Knife River lignite and Little Tonzona and Colstrip subbituminous lump coals, incubated for 3 days without prior saturation, achieved equilibrium-moisture values similar to that of the samples presaturated via the ASTM procedure. The effect of particle size on equilibrium moisture was more difficult to assess. Most of the forms for the Knife River and Colstrip coals attained similar equilibrium moistures after 3 days of incubation, regardless of coal size. Similar agreement was not achieved with the Little Tonzona coal in which the HWD- and SSD-lump-coal equilibrium moistures were considerably lower than their fine coal counterparts. In general, no particular coal form exhibited consistency of equilibrium moisture regardless of coal size.

Future Work

- Continue to develop the modified Jameson cell (9) to determine more accurately the relative dustiness of LRCs and dried LRCs.
- Continue to investigate equilibrium-moisture analysis with emphasis on various relative humidities, particle sizes, and incubation times.
- Conduct plant-site visits and coal sampling at coal mining and utility stations.
- Continue to correlate ASTM and modified procedures and to understand how they relate to "real-world" applications.
- Begin to investigate spontaneous combustion of raw and dried LRCs.

CONCLUSIONS

This report presents data for three raw coals and dried-coal products analyzed by various strength and stability test methods. The results show that as the moisture

content is decreased, the amount of generated dust substantially increased to levels viewed as unacceptable by industry (i.e., fines less than 0.5 mm not to exceed 10 wt%) (10). Tests performed to evaluate the tendency for moisture reabsorption of dried LRCs indicated that coals tend to reabsorb the moisture during air drying, whereas hydrothermal treatment processes do not allow reabsorption. Through development of these laboratory techniques, better predictions on the effects that transport, handling procedures, and climate have on the stability of dried LRCs are hoped. This is extremely important when marketing the virtues of a particular western coal type, as the coal is transported long distances to eastern or foreign markets. If commercial drying of LRCs is to be successful, efforts must continue on stability analysis and the development of cost-effective, stable products.

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TASK 4.0 ADVANCED FUEL FORMS AND COPRODUCTS

Subtask 4.1 Beneficiation for Advanced Systems

Oil Agglomeration

INTRODUCTION

New feedstock preparation processes for low-rank coals (LRCs) must achieve the irreversible removal of moisture, increase the coal Btu content, and yield a stable product not prone to spontaneous combustion, dustiness, or moisture reabsorption. These processes must also produce fuels that have a reduced propensity for fouling, thus requiring removal of troublesome inorganic species. Ion exchange of finely ground coal followed by oil agglomeration has the potential to accomplish these improvements as well as produce a fuel transportable by conventional methods.

The EERC has demonstrated that low-ash, low-sodium fuel can be produced by a combination of physical cleaning followed by chemical cleaning of fine coal (1-3). These clean coal products, however, are difficult to transport, handle, and store because of their high moisture content, fine size, and propensity toward oxidation. The EERC has demonstrated that the coal cleaning step can be combined with an oil agglomeration (coal recovery) step to produce a low-ash and -moisture, high-heating-value fuel.

The past year's investigations included the selection of agglomerating oil, the recovery of oil from agglomerates and process water, the assessment of agglomerate strength and stability, and preparation of a preliminary plant design and magnitude economic evaluation. Several process modifications were studied including the reduction of sodium in LRCs via carbonic acid treatment, the elimination of ion-exchange and process-water-pH treatments, and the selective reduction of minerals (ash-forming) coal species.

Background

The EERC oil-agglomeration process is divided into two steps: acid cleaning followed by fine coal aggregation (via oil agglomeration). The first step functions to reduce the content of inorganically associated elements such as sodium and calcium. Because the process is operated in a batch mode, the level of inorganic reduction is primarily a function of initial acid (H^+) concentration. In the second step, the fine coal is aggregated to produce a more easily handled fuel form. Aggregation also separates the eluted inorganic species from the clean coal.

In the EERC agglomeration process, LRCs are typically pulverized to a 30-mesh top size and then slurried in a dilute acid solution, usually at one part coal to two parts acid solution. The coal-acid solution is stirred for a maximum of 5 minutes at 5000 to 6000 rpm using a high-shear mixer. A suitable oil is then added to the coal-acid slurry. Low-shear mixing facilitates wetting of the coal by the oil, and agglomerates are formed due to repeated collisions of the oily coal particles. Agglomerate size is affected by oil concentration, vessel geometry, mixing speed and time, and oil type. The green

agglomerates are separated from the process water by screening and then are allowed to air dry for up to 24 hours prior to analysis and/or testing.

In previous work, the EERC demonstrated that strong acids, for example nitric, hydrochloric, and sulfuric, can reduce the ash content by up to 70 wt% in lignites and up to 50 wt% in subbituminous coals. Sodium and calcium reductions have exceeded 90 and 50 wt%, respectively, using solution concentrations ranging from 0.75 to 3.0 M (4,5) wt% acid.

The EERC has also investigated a range of coal- and petroleum-derived tars, oils, and residues for agglomerating LRCs. Ultimate analysis and open-column chromatography have been used to elucidate the oil characteristics that promote agglomeration (6,7). Further, the EERC demonstrated process modifications that allow utilization of poor agglomerating oils (6,7).

Oils suitable for low-shear LRC agglomeration have included coal-gasification-derived crude phenol, cresylic acid, and *m*-cresol (6,7). Agglomeration with these oils was typically complete within 5 to 10 minutes and high coal recovery (>90 wt%) was achieved at oil-coal ratios between 0.8:1 and 1:1. Preferred agglomerating oils have oxygen content (>10 wt%) and high polar-functionality content (>80 wt%) relative to ineffective agglomerating oils. At low-shear agglomerating conditions used crankcase oil, liquefaction tars and oils, mild gasification tars were ineffective for LRC agglomeration. These oils can, however, be induced to agglomerate LRC's by high-shear mixing, surfactant addition (e.g. crude phenol), or oil dissolution in a polar solvent (e.g. butanol).

The EERC oil-agglomeration process was successfully demonstrated in previous work using brown coal from Australia, lignites from North Dakota, Texas, and the Czech Republic, and subbituminous coals from Montana, Wyoming, and Alaska (4-6).

The EERC has investigated analysis methods for determining the moisture and oil contents of green, air-dried, and thermally deoiled agglomerates (4-6,8). Azeotropic distillation and Karl Fisher analysis were effective for determining the moisture content. Solvent extraction using methylene chloride or THF was effective for determining the oil content of green and air-dried agglomerates, although the solvent techniques could not completely elute residual oil from thermally treated agglomerates.

Thermal treatment of air-dried agglomerates, to recover agglomerating oil and to produce agglomerates for strength testing, has been investigated using batch, fixed-bed deoiling (in tube furnaces and autoclaves), and batch, fluid-bed deoiling. The processes were hindered by inadequate temperature control and heat distribution, inadequate oil-water condensation and recovery, and inadequate agglomerate treatment capacity.

Preliminary experiments have indicated that raw or chemically treated coal can be used to reduce the residual oil in the agglomeration process water (6). This use of coal is advantageous because it reduces oil loss and reduces the complexity of the water treatment process.

OBJECTIVES

The objectives for the past year were to complete tests in the areas of agglomerating oil testing and selection, oil recovery (from agglomerates and process water), and product stability (strength, dust generation, and moisture reabsorption). Additional objectives included the design and the economic evaluation of a commercial plant utilizing the EERC coal cleaning-oil-agglomeration process.

ACCOMPLISHMENTS

Testing and Selection of Agglomerating Oil

Two coal gasification-derived materials, tar oil and tar-oil lights, were investigated for their suitability as agglomerants for LRCs. Both oils were obtained from the Dakota Gasification Company, which operates the Great Plains synfuels plant in Beulah, ND. The tar oil contains benzene, toluene, xylene (BTX), cresylic acids, and creosote (56 wt%). The tar-oil lights is an experimental derivative produced by distillation of tar oil at 235°C. Separation of the tar oil into salable BTX and cresylic acid components and a creosote fraction is being evaluated by the Dakota Gasification Company (9,10).

Tar oil was successfully used as an agglomerant with Spring Creek and Colstrip subbituminous coals and with Beulah lignite at low-shear agglomerating conditions. The compatibility of tar oil and LRC resulted from the polar (phenolic, etc.) components of the oil that were present in sufficient quantity to cause agglomerate formation. The creosote fraction, however, was presumed to be responsible for the excessive oily appearance of the green and air-dried agglomerates and for the reduced integrity of the air-dried agglomerate relative to the agglomerate integrity of the crude phenol-LRC mixture.

The tar-oil lights, in contrast, failed to agglomerate treated or untreated coals at low-shear conditions. Catalyzed polymerization of the phenolic and polar components was hypothesized to have occurred during long-term storage, thus reducing the polar component concentration and inhibiting agglomerate formation. Tar-oil lights, however, were suitable for aiding in agglomerate growth when blended with other polar oils. Similarly, the tar-oil lights were induced to agglomerate LRCs by blending with polar solvents. The polar oils included crude phenol, cresylic acid and *m*-cresol. The solvents included methanol, ethanol, 2-propanol, and 1-butanol.

Agglomerates produced with a polar oil and the tar-oil lights were typically larger and qualitatively stronger, after air drying, than agglomerates produced without tar oil lights. The maximum tar-oil lights:coal was determined to be 1:2, after which further oil addition resulted in agglomerate degradation.

Three large batches of agglomerates were prepared from Spring Creek subbituminous coal for subsequent thermal deoiling and strength and stability evaluations. Test 1 agglomerates were prepared with 44 wt% of crude phenol and 48 wt% of tar-oil lights, and Test 2 agglomerates were prepared with wt% of crude phenol and 48 wt% of tar-oil lights. The oil content of the air-dried Test 1 agglomerates was determined to be approximately 32 wt%. Test 3 agglomerates were prepared with 80 wt% of crude phenol and 10 wt% of tar-oil lights; the oil content of air-dried Test 3

agglomerates was determined to be 29.3 wt%. Thermal deoiling and strength and stability evaluations are discussed in following sections.

Oil Recovery

Thermal Treatment Testing of Agglomerates

The primary purpose of thermal deoiling was to produce low-oil-content agglomerates for strength and stability evaluations. The system used for deoiling agglomerates was depicted and described elsewhere (4). Briefly, air-dried agglomerates were weighed and charged to the annulus of a wire-mesh basket; the annular configuration was intended to aid circulation of the flushing gas and improve heat transfer to the agglomerates. The basket and agglomerates were heated in a 2-gallon autoclave equipped with agglomerate temperature monitoring and heater control.

A continuous nitrogen purge prevented agglomerate combustion and carried vaporized oils and water from the autoclave. Oil and water were recovered using a primary condenser and a secondary condenser-knockout pot recovery train. Noncondensables were vented to the atmosphere in all tests. Deoiled agglomerates and condensate were recovered and weighed after cooldown.

Spring Creek Test 1 and Test 2 agglomerates (described in the previous section) were thermally treated at 310°C (590°F) for 60 minutes. The primary and secondary condensers were maintained at 18°C (65°F) and 0°C (32°F), respectively. Spring Creek Test 3 agglomerates were thermally treated at 230°C (446°F) and 260°C (500°F); the residence time at temperature was 30 minutes in both tests. The primary and secondary condensers were maintained at 0°C (32°F) and a cold-finger trap, immersed in liquid nitrogen, was used as a final knockout.

The deoiled agglomerate and condensed oil-water mass from Tests 1 and 2 at 310°C (590°F) comprised only 83.8 and 90.3 wt%, respectively, of the initial agglomerate charge. The variation in agglomerate and oil-water recoveries were presumed to have been the result of several factors, including insufficient condenser-train cooling capacity, coal devolatilization at the high deoiling temperature, and/or partial gasification (via thermal degradation) of the agglomerating oil. Modification of the deoiling and condensation operating conditions and thermal treatment at lower temperatures resulted in a greater mass recovery of agglomerates and condensables. The deoiled agglomerate and condensed oil-water mass from Test 3 agglomerates treated at 230°C (446°F) and 260°C (500°F) comprised 98.1 and 94.7 wt%, respectively, of the initial agglomerate charge.

Because solvent extraction was considered to be unreliable for directly determining the oil content of thermally treated agglomerates, the residual oil contents were calculated from the air-dried agglomerate oil content and the agglomerate mass loss. The oil content of the deoiled Test 1 agglomerates was less than 1 wt%; similarly, the oil contents after deoiling the Test 3 agglomerates at 230°C (446°F) and 260°C (500°F) were 5.0 and 3.0 wt%, respectively.

Process Water Adsorption Testing

A coal adsorption technique was evaluated for reducing the oil content of agglomeration process water. Oily process water, obtained from a Spring Creek subbituminous coal agglomeration experiment, was mixed with -100-mesh Spring Creek coal in a 1:1 water-to-coal weight ratio. The slurry was blended for 10 minutes and then the process water was recovered by filtration. The procedure was repeated at a 1.3:1 water-to-coal ratio with a new aliquot of coal. The initial oily water and the intermediate and final filtrates were analyzed for total carbon (TC) content. The TC concentration (in mg/L) for each water fraction was multiplied by 1.30 (grams oil/gram carbon in the oil) to normalize to an oil concentration (in mg/L).

In a single adsorption test, the process-water-oil concentration was reduced by 87.5 wt% after the initial adsorption treatment and 98.0 wt% after the final adsorption treatment; the initial, intermediate and final process-water-oil concentrations were 16,900, 2120, and 340 mg/L, respectively. The results indicated that this technique could possibly be used as an effective replacement for solvent extraction to recover phenolic and polar oils from water.

Product Strength and Stability Testing

Air-dried and thermally deoiled agglomerates were evaluated for strength via drop-shatter and tumble (abrasion) testing. Shatter-resistance testing was performed by dropping an agglomerate charge from a height of 6 feet through a PVC pipe into a stainless steel vessel. The vessel, with a ½-inch-thick bottom, was used to retain the agglomerates and prevent material loss. The agglomerates were dropped ten times and screening was performed after the second, sixth, and tenth drops. Abrasion-resistance testing was performed using a stainless-steel vessel with dimensions equivalent to an ASTM D441 coal-tumbling apparatus. The spacing between the lifting shelves and vessel wall was obstructed to ensure that the agglomerates were continually lifted and dropped. Agglomerates were tumbled for 30 minutes at 40 rpm.

Select samples of the thermally deoiled agglomerates were evaluated for stability toward moisture reabsorption. In the first stability test, agglomerates were weighed, immersed in water, recovered by screening, and then air-dried. The mass increase due to permanent moisture reabsorption was then determined. In the second stability test, deoiled agglomerates were subjected to ASTM equilibrium-moisture test conditions of 96%-97% relative humidity. After attainment of constant mass, the agglomerates were removed from the incubation chamber and were immediately analyzed for moisture content via Karl Fisher analysis.

Air-Dried Agglomerate Evaluation

The size distributions of pre- and post-strength-tested agglomerates, from Test 1 described previously, are presented in Table 4.1-7. Agglomerates were manually screened to minimize separation of clumped agglomerates into discrete agglomerates. The most significant results of drop and tumble testing were twofold: only minimal degradation of agglomerates occurred, and fine-coal (-30-mesh) generation was minor. The primary cause of the change in size distribution was the cleavage of the clumped agglomerates at the weaker contact or bridging points. The distinct agglomerates were typically larger

TABLE 4.1-7

Drop- and Tumble-Strength Results for Test 1
Air-Dried Agglomerates (Cumulative wt% Larger)

Screen Opening, inches	Tumble Testing		Drop Testing			
	Initial	Final	Initial	2 Drops	6 Drops	10 Drops
0.25	45.7	20.8	36.7	21.0	12.2	12.1
0.187	61.3	41.3	54.1	39.5	34.0	33.0
0.132	87.0	72.8	80.3	72.8	71.8	71.1
0.0787	98.5	91.1	97.2	95.1	95.1	95.1
0.0232	99.7	96.0	99.5	98.2	99.0	99.0

than 6-mesh (0.132"). The most significant breakup of the clumped agglomerates occurred during tumble testing. The fine coal that was produced during strength testing also had diminished adhesive properties relative to that of the raw coal fines, since the oiled coal fines did not tend to stick to the tumble and drop vessels, screens, or other test equipment.

Deoiled Agglomerate Evaluation

Deoiled agglomerates from Tests 1, 2, and 3 were evaluated for strength via the drop-shatter and tumble (abrasion) tests. The size distribution prior to and following drop and tumble testing are presented in Tables 4.1-8 and 4.1-9 for Tests 1 and 2 deoiled agglomerates. Preliminary results indicated that the deoiled agglomerates were inferior, relative to the air-dried agglomerates. Subjecting the deoiled agglomerates to drop and tumble testing resulted in the breakup of clumped agglomerates and the degradation of agglomerates into fragments and fine coal (< -30 mesh). Similar to that from testing of the air-dried agglomerates, tumble testing produced the most significant agglomerate degradation. Approximately 20 wt% of the agglomerates, from deoiling tests at 310°C, were reduced to under 30 mesh (0.0232"). The most probable cause for the poor agglomerate integrity was the excessive thermal treatment temperature, which resulted in insufficient agglomerate oil content as well as physical changes in the coal.

The size distribution prior to and following drop and tumble testing are presented in Tables 4.1-10 and 4.1-11 for Test 3 agglomerates deoiled at 230°C (446°F) and 260°C (500°F). The results of drop-shatter and tumble testing indicated that lowering the thermal treatment temperature did not improve the agglomerate strength. The strengths of the Test 3 agglomerates after thermal treatment were inferior to those of the Tests 1 and 2 deoiled agglomerates. The most probable explanation for the decreased strength lay with the lower tar-oil-light concentration used during Test 3 agglomerate preparation.

Test 3 deoiled agglomerates were subjected to the moisture immersion test for 3.5 months. During immersion testing, essentially no fines were produced, and all

TABLE 4.1-8

Drop- and Tumble-Strength Results for Test 1
Deoiled Agglomerates (Cumulative wt% Larger)

Screen Opening, inches	Tumble Testing		Drop Testing			
	Initial	Final	Initial	2 Drops	6 Drops	10 Drops
0.25	15.0	2.5	23.8	11.8	2.8	2.4
0.187	31.2	12.4	44.7	30.6	20.0	14.3
0.132	66.7	42.7	79.5	69.1	57.8	49.1
0.0787	96.8	74.9	98.1	94.9	88.7	81.7
0.0232	99.7	82.3	99.5	98.2	95.9	92.1

TABLE 4.1-9

Drop- and Tumble-Strength Results for Test 2
Deoiled Agglomerates (Cumulative wt% Larger)

Screen Opening, inches	Tumble Testing		Drop Testing			
	Initial	Final	Initial	2 Drops	6 Drops	10 Drops
0.25	23.5	6.0	33.5	17.6	8.4	7.7
0.187	57.5	26.3	70.3	54.5	43.5	39.7
0.132	90.0	62.1	90.7	84.3	75.0	69.5
0.0787	99.9	79.8	97.2	96.2	90.9	87.2
0.0232	99.9	81.1	98.3	97.9	95.1	93.0

agglomerates retained their initial form and size. The interior of immersed agglomerates showed no evidence of water saturation. Only a slight discoloration of the water occurred during immersion testing with the 230°C (446°F) deoiled agglomerates. After approximately 18 hours of air drying, the 230°C (446°F) and 260°C (500°F) agglomerates weighed only 1.5 wt% and 1.9 wt% more, respectively, than the preimmersion agglomerates.

Test 3 deoiled agglomerates were also subjected to equilibrium-moisture testing. After 4 days of incubation, the deoiled agglomerate mass gain was less than 0.2 wt%

TABLE 4.1-10

Drop- and Tumble-Strength Results for Test 3 – 230°C
Deoiled Agglomerates (Cumulative wt% Larger)

Screen Opening, inches	Tumble Testing		Drop Testing			
	Initial	Final	Initial	2 Drops	6 Drops	10 Drops
0.25	20.8	1.6	24.8	13.6	6.0	2.8
0.132	63.9	14.1	65.1	50.1	32.0	22.1
0.0787	91.3	23.1	91.3	79.7	62.6	52.0
0.0469	98.1	30.3	98.4	90.4	77.4	67.1
0.0331	98.6	32.8	98.7	92.3	81.0	71.9

TABLE 4.1-11

Drop- and Tumble-Strength Results for Test 3 – 260°C
Deoiled Agglomerates (Cumulative wt% Larger)

Screen Opening, inches	Tumble Testing		Drop Testing			
	Initial	Final	Initial	2 Drops	6 Drops	10 Drops
0.25	18.4	1.1	22.6	14.3	6.0	3.7
0.132	56.4	11.8	67.5	52.2	34.8	24.3
0.0787	89.9	23.1	92.1	80.6	63.7	53.9
0.0469	97.3	33.5	98.7	90.7	77.8	69.5
0.0331	98.1	36.8	99.3	92.3	80.9	73.5

(based on the initial sample weight), thus indicating a near-equilibrium condition. The moisture contents at equilibrium were determined to be 5.7 and 5.4 wt%, respectively, for the 230°C (446°F) and 260°C (500°F) deoiled agglomerates.

Agglomeration Process Modifications

Carbonic Acid Coal Cleaning

Carbonic acid treatment of LRCs at elevated pressures was tested as a potential lower-cost option for the preagglomeration treatment of LRCs to reduce sodium content. Carbonic acid treatment was performed in a batch mode using a stainless steel 2-gallon autoclave system that has been described elsewhere (4). Briefly, a slurry consisting of pulverized coal (-60 mesh) and deionized water was charged to the autoclave, after which the system was pressurized to the desired level with carbon dioxide (CO₂). The slurry was continuously agitated to enhance solubilization of the CO₂ and to improve coal and carbonic acid contact. After treatment, the system was depressurized and the slurry recovered for analysis.

Two high-sodium North Dakota lignites (Knife River and Gascoyne) and a high-sodium Montana subbituminous coal (Spring Creek) were selected for treatment. The moisture-free (mf) ash contents of the raw Knife River, Gascoyne, and Spring Creek coals were 10.2, 9.7, and 4.95 wt%, respectively. The sodium oxide contents (SO₃-free) of the ASTM coal ashes were 10.5, 11.2, and 9.5 wt%, respectively. The effect of residence time was evaluated by varying mixing time from 30 to 120 minutes, and the effect of coal concentration was evaluated by varying the coal-water ratio from 1:5 to 1:10. The headspace pressure above the coal slurry was maintained at 85 psig in each test.

Carbonic acid treatment produced modest reductions in ash content for all three coals. The highest ash reduction, 17.3 wt%, was achieved with the Knife River lignite at a 1:10 coal-water ratio. Maximum ash reductions of 13.5 and 12.3 wt%, respectively, were achieved with the Gascoyne lignite and the Spring Creek subbituminous at the same coal-water ratio. Baseline testing without carbonic acid did not significantly reduce the ash content of the coal. Removal of sodium was the predominant cause of the decrease in ash contents. The sodium reductions for the Knife River, Gascoyne, and Spring Creek were 63, 80, and 72 wt%, respectively.

Increasing the coal-to-water ratio impaired the removal of inorganics, probably because decreasing the water volume resulted in less solubilization of CO₂ and less production of H⁺ for ion exchange. Doubling the coal:water ratio decreased the ash removal from the Knife River lignite by almost 50%.

Selective Agglomeration

Selective agglomeration was investigated for separating the mineral-rich (high ash) and clean-coal (low ash) fractions. This process relies on differences in the affinity of the coal and minerals for the agglomerating oil to effect inorganic reduction. Selective agglomeration, when combined with ion exchange, was considered applicable for producing low-fouling fuels for conventional utility applications or, possibly, a very low-ash fuel for advanced power systems.

The test coals included Spring Creek (carbonic acid-treated) and Colstrip subbituminous coals and Knife River and Beulah lignites. The subbituminous coals and the Knife River lignite were pulverized (dry) to 100-mesh top size, and Beulah lignite was

pulverized to 60-mesh top size. The mf ash contents of the Spring Creek, Colstrip, Knife River, and Beulah were 4.8, 14.0, 10.1, and 7.8 wt%, respectively.

Crude phenol was used as the primary agglomerating oil; a supplemental test used tar oil. The agglomerating oil-to-coal ratio was varied in each test. Agglomerates produced with -100-mesh coal were separated from tailings and process water using a 100-mesh screen and a 60-mesh screen was used when agglomerating -60-mesh coal. Tailings were recovered from the process water via vacuum filtration. The agglomerates and tailings were air dried overnight, and each was analyzed for ash content.

The conditions and results of selective-agglomeration testing are presented in Table 4.1-12. Preliminary results indicated that only Colstrip was substantially improved by selective agglomeration, as indicated by comparing the tailing ash contents with those of the raw coal and agglomerate. The relatively few tests with the Spring Creek subbituminous coal and the Beulah and Knife River lignites preclude judgment on their amenability to selective agglomeration for ash reduction, although the low ash content of the tailings indicated inadequate concentration of ash in this fraction.

TABLE 4.1-12

Selective-Agglomeration Test Conditions and Results

Test Coal	Oil:Coal Ratio	Agglomerates		Tailings	
		Recovery, wt%	Ash, wt%	Recovery, wt%	Ash, wt%
Colstrip	1:10	34.7	7.10	65.3	13.4
	2:10	58.1	7.2	41.9	15.9
	3:10	68.9	6.6	31.2	19.5
	4:10	72.8	6.9	27.2	19.4
	5:10	87.7	6.6	12.3	28.3
	3:10 ¹	63.0	6.4	37.0	14.0
	5:10 ¹	68.8	4.7	31.2	15.0
Spring Creek	5:10	85.1	3.1	14.9	5.0
Knife River	4:10	32.0	5.7	68.0	7.8
	5:10	34.0	5.2	66.0	7.6
	6:10	44.0	5.5	56.0	8.0
	7:10	46.2	5.1	53.8	7.9
Beulah	5:10	85.5	3.9	14.5	6.7

¹ Tar oil used as the agglomerant.

Air-dried Colstrip subbituminous agglomerates produced at the 5:10 oil-to-coal ratio had moisture and oil contents of 8.8 and 16.3 wt%, respectively. An ash balance indicated that 91.5 wt% of the raw coal ash was accounted for in the agglomerates and tailings. Conservatively estimated, over 87 wt% of the maf raw coal was recovered as agglomerates, while only about 65 wt% of the raw coal ash ended up in agglomerates. The ash contents of the air-dried agglomerates and the moisture- and oil-free (THF extracted) agglomerates were 6.6 and 8.6 wt%, respectively.

The suitability of selective agglomeration for sulfur reduction (via pyrite removal) was also investigated. The moisture-free sulfur contents of the raw Colstrip coal was compared with the moisture- and oil-free sulfur content of the Colstrip agglomerates described above. The sulfur contents, 0.56 and 0.51 wt%, respectively, differed only slightly; the variance was probably within experimental and analytical error. Consequently, selective agglomeration was considered to have minimal effect on sulfur reduction with the coal studied.

Agglomeration without Coal Pretreatment or Slurry pH Adjustment

The ability of polar oils to agglomerate LRCs using the EERC low-shear agglomeration process had been hypothesized to be aided by the removal of coal ion-exchangeable species and by the presence of acid cations during the agglomeration step. The two tenets of this hypothesis were: 1) removal of inorganic elements modifies the coal surface and increases wettability by the agglomerating oil, and 2) a low-pH (< 2) coal slurry aids displacement of coal surface- and pore-moisture by the agglomerating oil via a mechanism similar to that of osmosis.

Two scenarios, however, would make acid cleaning and/or agglomeration in a low-pH slurry disadvantageous in the operation of a commercial agglomeration plant. Firstly, ion exchange may not be necessary for low-sodium (or low-ash) coals or for fine-coal recovery and, secondly, process water containing both residual acid and residual agglomerating oil would be difficult and costly to treat. In a commercial plant, it would be necessary to maintain separate water paths and treatment schemes for the ion-exchange and oil-agglomeration circuits.

Two modified agglomeration procedures were successfully demonstrated using two subbituminous coals (Spring Creek and Colstrip, MT) and two lignites (Knife River and Beulah, ND). Firstly, raw Colstrip, Beulah, and Knife River were slurried in deionized water at a 1:2 coal-to-water ratio and, without acid treatment, the coals were agglomerated using the crude phenol or tar oils. The oil volumes (~ 1 mL oil:1 gram as-received coal) and the mixing time (~ 5 minutes) required for agglomeration were essentially equivalent to those values required for agglomerating acid-treated coals.

Similarly, Spring Creek subbituminous treated with carbonic acid was successfully agglomerated in a neutral-pH water solution using polar agglomerating oils (e.g. crude phenol).

Plant Design and Economic Evaluation

Design Basis and Assumptions

A commercial coal cleaning-oil-agglomeration plant was designed based on observations and data obtained from bench-scale test efforts. The resulting economic analysis provided only a magnitude estimate (± 30) of the actual process costs.

The plant is located at the Spring Creek (subsidiary of NERCO Coal Corp.) coal mine in the northern part of the Powder River Basin. The mine, which produces a low-ash, high-sodium subbituminous coal, is located in Big Horn County of Southern Montana. The results of proximate, ultimate, heating value, and ASTM ash analyses for the raw Spring Creek coal are presented in Table 4.1-13.

The nominal capacity of the plant is 3.33 MMt/yr of run-of-mine (ROM) coal (input). Approximately 90% of the input coal load is directed to the coal cleaning-oil-agglomeration process and the balance to process heat generation. The plant produces 2.36 MMt/yr of a low-ash, low-sodium, high-heating-value lump fuel. The ash and sulfur contents and the heating value of the product (deoiled) agglomerates are 3.1 wt%, 0.53 wt%, and 12,700 Btu/lb, respectively. The moisture content of the final product (deoiled) agglomerate is below 0.5 wt% and the theoretical uncontrolled sulfur emission is 0.83 lb SO₂/MMBtu.

Process Description

The block flow diagram (Figure 4.1-5) of the coal cleaning-oil-agglomeration plant shows the major processing areas including facilities for feed-coal handling and preparation, coal treatment and agglomeration, product storage and loadout, and waste-

TABLE 4.1-13

Proximate and Ultimate Analysis for Spring Creek Raw Coal

Analysis	wt%
As-Received Moisture	25.3
Proximate, mf	
Volatile Matter	44.2
Fixed Carbon	50.7
Ash	5.1
Ultimate, mf	
Carbon	72.9
Hydrogen	5.2
Nitrogen	0.8
Sulfur	0.56
Oxygen	15.5

Figure 4.1-5 Block flow diagram for low-rank coal agglomeration plant.

stream treatment and disposal. The five major areas are: Feed-Coal Receiving and Storage (100), Slurry Preparation and Ion Exchange (200), Oil Agglomeration (300), Thermal Deoiling and Oil Recovery (400), and Process Effluent Control (500). A description of each process area follows.

Coal is crushed in-pit to a 6" top size and then delivered to Area 100 of the plant for stockpiling. The coal is then reduced in the primary crusher and hammermill crusher. Screening removes the +30-mesh coal which is redirected to the size-reduction circuit. A coal sampling system and surge (bin storage) capacity are provided.

The crushed coal (-30 mesh) is transferred via enclosed conveyor to Area 200 where makeup water and recycled, ion-exchange-process water are added to produce a slurry. The solids concentration is approximately 25 wt% based on a free water-to-coal ratio of about 2:1. The coal slurry is transferred to the ion-exchange system where makeup concentrated nitric acid is added to raise the acid concentration to 3 wt%. Slurry preparation and ion exchange are performed in continuously stirred tank reactors. After a 2-minute residence time for ion exchange, the slurry is dewatered via screen bowl centrifugation. The centrate, containing residual acid and eluted coal inorganics, is then split: 90 wt% of the stream is recycled to the slurry preparation area and 10 wt% (blowdown) is directed to effluent control (water treatment). Blowdown of the ion-exchange-process water is necessary to prevent readsorption of the eluted cations by the coal.

Wet centrifuge cake (clean coal) from the ion-exchange process is conveyed to Area 300 and discharged onto high-speed dewatering screens. Recycled process water containing 16,800 mg/L oil is sprayed onto the coal to facilitate adsorption of the residual bridging oil. The bridging oil concentration in the water is reduced by 99 wt%. The dewatering screen underflow (-100-mesh coal and process water) is pumped to a belt filter press; the filter cake is combined with the high-speed, dewatering-screen, coarse-coal discharge. The process water containing approximately 170 mg/L bridging oil is blowdown to the process effluent-control area.

The oiled, clean coal is conveyed to slurry preparation in Area 300, where the balance of the recycled, oily process water is added. The slurry is then pumped to the oil-agglomeration circuit. Makeup binding oil plus bridging oil and water recovered from agglomerate thermal treatment are added; the oil-to-coal ratio is maintained at 0.85:1.0. Agglomerates are formed in baffled, continuously stirred tank reactors, and then are discharged from the top of the reactor, and dewatered on 28-mesh-sieve bend screens. The screen underflow is split, 65 wt% is pumped to slurry preparation and 35 wt% is pumped to residual bridging oil adsorption. Because the process is a net water producer, water (preferentially the least contaminated) must be removed from the process. The mass rate of process water directed to residual bridging oil adsorption is equivalent to the mass rate of the inherent plus surface coal moisture, where the surface moisture is that remaining from the ion-exchange circuit.

Green agglomerates are conveyed to Area 400 for thermal treatment and bridging oil recovery. The green agglomerates are fed via vibratory conveyers into rotary-steam-tube driers (operated at approximately 230°C [446°F]) where bridging oil and water are vaporized. Binding oil remains on the agglomerates and provides strength and resistance to moisture reabsorption. The bridging oil and water are condensed and then returned to

Area 300 agglomeration; noncondensables are flared. Saturated steam for the tube drier is provided by coal-fired process heaters. Deoiled agglomerates are conveyed to storage and product loadout. Ash produced in the fired heaters from combustion of Spring Creek coal is landfilled in the mine.

Treatment of blowdown, ion-exchange-process water and blowdown, agglomeration-process water is provided in Area 500. The ion-exchange-process water is neutralized and then treated by reverse osmosis to produce a concentrated mineral stream. Powdered activated carbon (PAC) is used to remove residual bridging oil from the agglomeration-process water. The discharge water streams are deep-well injected.

Cost Estimation and Financial Analysis Criteria

Agglomeration testing was performed only in a batch mode on a bench scale, and agglomeration in a larger continuous process will undoubtedly introduce many direct scaleup difficulties. Principal among these difficulties will be continuous agglomeration in a stirred tank reactor and screening and conveying of green agglomerates without causing significant degradation. Adsorption of bridging oil from agglomeration process water with coal was viable with bench-scale testing, but the proposed method for the commercial plant is untested. Additional uncertainties include rotary-steam-tube drying to thermally treat (deoil) the green agglomerates. The major difficulties in thermal deoiling will include minimizing exposure of the agglomerates and oil vapor to air. Rotary-steam-tube drying was chosen because this unit operation is a proven technology for handling very wet solids, and for solvent recovery (11). Steam tube drying is also effective for applications where air infiltration must be minimized or eliminated.

Another significant presumption for the design of this plant is the availability of bridging and binding oils for agglomeration. Presently, only the Great Plains synfuels plant located in Beulah, North Dakota, produces sufficient quantities of polar oils (crude phenol and tar oil) that are suitable for LRC agglomeration. The oils, however, have considerable value to Dakota Gasification as fuel (for steam generation) and recovery of marketable chemicals. Even the residue from by-product recovery, which could be a suitable binding oil, has higher value as a fuel. Further, this plant design presumes that both a bridging oil (with a final boiling point of 230°C) and a binding oil (creosote from tar-oil fractionation) are available.

Equipment for all areas of the plant are commercially available. Equipment exposed to acid or acidic coal slurries are available in stainless steel materials of construction. Equipment was sized using the material flow rates presented in Table 4.1-14. The major sources of equipment cost estimates included vendor estimates, in-house data, coal-cleaning cost models (12), and coal-cleaning plant designs and economic evaluations prepared by others (13,14). All equipment costs were updated to 1993 dollars using the Chemical Plant Cost Index.

Evaluation of the direct plant cost was based on factored cost estimates or vendor quotes for individual equipment in each area of the plant. The total capital cost, comprised of total plant cost and working capital, for the proposed commercial plant is presented in Table 4.1-15. The factors used to determine installation, piping, electrical, engineering and fees, construction, contingency, etc. are also presented in Table 4.1-15.

TABLE 4.1-14

Oil-Agglomeration Process Material Balance (ton/hour)

Stream Number	1	2	3	4	5	6	7	8
Total Flow Rate	476.2	47.6	428.6	675.1	157.6	1261.3	24.6	1285.9
Solids Rate	355.7	35.5	320.2	0.0	0.0	320.2	0.0	320.2
Water	120.5	12.1	108.4	664.7	157.6	930.7	0.0	930.7
Oil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acid	0.0	0.0	0.0	10.4	0.0	10.4	24.6	11.6
Stream Number	9	10	11	12	13	14	15	16
Total Flow Rate	535.8	750.1	75.0	219.3	215.6	539.5	416.3	955.8
Solids Rate	320.2	0.0	0.0		0.0	320.2	0.0	320.2
Water	215.6	738.5	73.8	215.6	215.6	215.7	409.3	625.0
Oil	0.0	0.0	0.0	3.69	0.0369	3.65	6.99	10.64
Acid	0.0	11.6	1.16		0.0	0.0	0.0	0.0
Stream Number	17	18	19	20	21	22	23	
Total Flow Rate	615.0	1570.8	635.6	935.2	336.9	598.3	16.70	
Solids Rate	0.0	320.2	0.0	320.2	320.2	0.0	0.0	
Water	261.4	886.4	624.9	261.5	0.0	261.5	0.0	
Oil	353.5	364.2	10.68	353.5	16.66	336.8	16.70	
Acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	

TABLE 4.1-15

Capital Costs for 2,360,00-tons/year LRC Agglomeration Plant

	1993 Costs
Delivered Equipment Costs:	
Area 100 Feed-Coal Receiving and Storage	4,320,295
Area 200 Slurry Preparation & Ion Exchange	5,829,612
Area 300 Agglomeration	4,020,631
Area 400 Thermal Deoiling	32,072,385
Area 500 Process-Effluent Control	12,280,435

A. Total Delivered Equipment	58,523,358
Other Direct Costs	
Installation (30% of A)	17,557,007
Instrumentation (20% of A)	11,704,672
Piping (20% of A)	11,704,672
Electrical (20% of A)	11,704,672
Paint and Insulation (5.0% of A)	2,926,168
Process Buildings & Land (30% of A)	17,557,007
Auxiliary Buildings (10% of A)	5,852,336
Site Development (40% of A)	23,409,343

B. Total Direct Cost	160,939,234
Engineering and Fees (15% of B)	
Construction and Contingency Fees (15% of B)	24,140,885
Contingency (20% B)	24,140,885
	32,187,847

C. Total Indirect Cost	80,469,617
D. Total Plant Cost (B+C)	241,408,851

E. Working Capital (20% of D)	48,281,770

F. Final Total Capital Cost (D+E)	\$289,690,622

A summary of the annual operating costs, for the base case scenario described above, is presented in Table 4.1-16. The direct operating costs were estimated using the salary, water, coal, electricity, acid, and agglomerating oil costs presented in Tables 4.1-17 and 4.1-18. The binding oil concentration on the product agglomerates is 5 wt% for the base case plant. The binding oil and makeup bridging oil costs are estimated to be equivalent to the fuel value (\$100/ton) of the crude phenol and tar-oil streams. The acid concentration for the base case is 3.0 wt%.

TABLE 4.1-16

Operation Cost for Conceptual 2,360,000-tons/year
LRC Agglomeration Plant

Type of Coal:	Deoiled Agglomerates		
Moisture in Raw Coal, %	25.3		
Oil in Agglomerates, %	5.0		
Operating Days	292		
Heat Value, Btu/lb	12,700		
Variable Costs	\$/MMBtu ¹	\$/ton ¹	\$/year
A. Coal Preparation			
Coal at Mine	0.340	0.48	20,008,925
B. Labor			
Operations and Supervisor	0.133	3.38	7,987,200
Maintenance and Supervisor	0.047	1.20	2,839,200
Analytical	0.012	0.04	748,800
Other Labor Cost	<u>0.028</u>	<u>0.12</u>	<u>1,698,000</u>
Subtotal	0.221	4.75	13,273,200
C. Utilities			
Electricity	0.092	2.34	5,536,221
D. Reagents			
Waste Disposal	0.008	0.21	500,000
Wastewater Treatment	0.012	0.30	700,000
Nitric Acid	0.574	14.58	34,408,800
Oil Binder	<u>0.195</u>	<u>4.96</u>	<u>11,705,600</u>
Subtotal	0.789	20.05	47,314,400
Total Variable Costs	<u>1.437</u>	<u>35.63</u>	<u>86,132,746</u>
Fixed Costs:			
A. Depreciation (12% for 20 year)	0.519	13.18	31,098,288
B. General Maintenance	0.193	4.91	11,587,625
C. Overhead (1% of Capital Cost)	0.097	2.46	2,896,906
Total Fixed Costs	<u>0.809</u>	<u>20.54</u>	<u>45,582,820</u>
Operating Cost (Variable + Fixed)	<u>2.246</u>	<u>56.17</u>	<u>131,715,566</u>

¹ Deoiled agglomerate basis

TABLE 4.1-17

Salaries with Benefits of LRC Agglomeration Plant Personnel		
Job Category	Number	Wage
Area 100 Operators	12	\$50/hr
Area 200 Operators	12	\$50/hr
Area 300 Operators	12	\$50/hr
Area 400 Operators	15	\$50/hr
Area 500 Operators	9	\$50/hr
Shift Foreman	9	\$60/hr
Mechanical/Electrical	9	\$60/hr
Mechanics	9	\$55/hr
Electricians	6	\$55/hr
Laboratory Technicians	9	\$40/hr
Plant Managers	2	\$10,500/mo
Plant/Environmental Engineers	3	\$8,500/mo
Personnel/Safety Administration	6	\$6,500/mo
Purchasing/Warehouse Clerk	6	\$3,500/mo
Secretary/Clerk	10	\$3,500/mo
YEARLY TOTAL	129	

TABLE 4.1-18

Criteria for Direct Operating Costs of LRC Agglomeration Plant	
Raw Water Cost	\$0.05/1000 gallons
Coal Cost	\$6/ton
Electricity Cost	\$0.07/kWh
Acid (delivered)	\$200/ton
Agglomerating Oil	\$100/ton

The criteria for the financial analysis of the agglomeration process included 100% equity financing, 20-year plant life, declining rate depreciation with switch over to straight line, 15%-salvage value, 80%-plant load, and 15%-after-tax rate of return (AT ROR). A spreadsheet program was used to calculate the agglomerate selling price; by trial-and-error the agglomerate selling price for the freight-on-board (fob) plant was varied until the desired AT ROR equaled 15%.

For the base case scenario the selling price of the agglomerates is \$3.40/MMBtu, and approximately 66.2% or \$2.25/MMBtu is required to cover yearly operating costs. The major operating expenses for the plant are coal (\$0.334/MMBtu), nitric acid (\$0.574/MMBtu), labor (\$0.221/MMBtu), binding oil (\$0.195/MMBtu), and depreciation (\$0.519/MMBtu).

A sensitivity analysis was performed to determine the variation in agglomerate selling price with acid concentration, agglomerate-binding oil concentration, and agglomerating oil cost. Each independent variable was investigated at three levels, including the base case levels. Additional levels included acid concentrations of 0.75 and 0 wt%, agglomerating oil costs of \$10/ton and \$50/ton, and agglomerate-binding oil concentrations of 10 and 15 wt%.

At an acid concentration of 0.75 wt%, the objective would be to reduce primarily the sodium content of the coal prior to agglomeration. At an acid concentration of 0 wt%, coal inorganics would not be reduced, and the objective would be to prepare a stable, strong high-heating-value lump fuel. Oil agglomeration without acid cleaning could be employed for fine LRC recovery or for selective rejection of LRC minerals and pyritic sulfur. The higher agglomerate-binding oil concentrations were included, because these levels may be the appropriate range in which abrasion- and shatter-resistant agglomerates are achieved.

The economic evaluations were estimated for 27 different agglomeration processing scenarios based on the three levels of independent variables. The most significant influence on agglomerate selling price was the level of acid consumption. For example, using the same oil cost (\$100/ton) and agglomerate oil concentration (5 wt%) of the base case, the agglomerate selling price was \$2.36, \$3.05, and \$3.40/MMBtu, respectively, for acid concentrations of 0, 0.75, and 3.0 wt%. Increasing the oil concentration from 5 to 15 wt% increased product cost by up to \$0.45/MMBtu at the highest oil cost of \$100/ton. However, assuming that a very low cost binder (\$10/ton) could be obtained, increasing the oil concentration actually decreased the agglomerate selling price although the decrease was very modest (<\$0.10/MMBtu).

The capital, operating, and products costs are presented in Table 4.1-19 for three scenarios: 1) the base case, 2) 0-wt% acid and an oil cost of \$10/ton, and 3) 0-wt% acid and an agglomerate binding oil concentration of 15 wt%. At a binder cost of \$10/ton, an oil concentration of 5 wt%, and 0 wt% acid (no coal cleaning) an agglomerate selling price of \$2.19/MMBtu was obtained. This selling price is approaching the processing cost for other advanced LRC upgrading processes. At a binder cost of \$100/ton, an oil concentration of 15 wt%, and 0 wt% acid (Scenario 3), an agglomerate selling price of \$2.78/MMBtu was obtained.

Discussion

Investigations conducted this year included selection of agglomerating oil, recovery of agglomerating oil from agglomerates and process water, assessment of agglomerate strength and stability, and preparation of a preliminary plant design and economic evaluation. With respect to the various subtasks, several conclusions from testing were positive. First, thermally deoiled agglomerates have exceptional resistance to moisture reabsorption under water immersion and high humidity conditions. Secondly, pulverized coal can be used effectively as a primary treatment media for reducing the residual oil

TABLE 4.1-19

Variation of Capital, Operating, and Product Cost, with Acid Concentration,
Oil Cost, and Agglomerate-Binding Oil Concentration

Scenario	1	2	3
Capital Cost, \$	289,691K	232,270K	248,433K
Total Variable Cost, \$/MMBtu	1.437	0.620	1.283
Total Fixed Cost, \$/MMBtu	0.809	0.648	0.620
Operating Cost, \$/yr	134,612K	76,049K	127,600K
Product Selling Price, \$/MMBtu	3.40	2.19	2.78

content of agglomeration process water. This capability helps reduce the complexity and cost of the oil-agglomeration process as well as reducing the loss of agglomerating oil.

Several process modifications were investigated that improved the flexibility of the EERC oil-agglomeration process. Carbonic acid showed excellent potential as a replacement for strong acids and for the selective reduction of sodium in LRCs. Also, selective agglomeration showed potential for reducing the mineral content of one high-ash LRC.

However, preparation of a low-ash lump fuel using the EERC oil-agglomeration process is presently hindered by several factors. First, as with other oil-agglomeration processes, suitable oils are neither inexpensive nor plentiful in supply. Although, polar coal-derived oils including tar oil show exceptional compatibility with LRCs, these oils have higher value as chemical feedstocks or as fuel, making them too costly as an agglomeration feedstock. Second, the strengths of agglomerates containing up to 5 wt% of oil are insufficient to permit handling and transportation by methods employed with steam coals. Third, incorporating chemical cleaning is economically not feasible for producing a fuel for use as switching or blending feedstock in the steam coal market.

Several additional features of the EERC agglomeration process that contribute to the high capital and operating costs include the water solubility of the agglomerating oil and the high amounts of retained moisture of the green agglomerates. The water solubility of the oil necessitated costly water treatment and prohibits using the coal cleaning-oil-agglomeration process for concurrent coal and oil upgrading, a feature which could greatly enhance the process economics. Also, because the moisture-to-solids ratio for the green agglomerates is higher than that of the raw coal, a proportionally greater heat load and heat-transfer area (more equipment) are required to produce a fuel with equal moisture content from the green agglomerates.

Near-term potential for the EERC process may exist for the preparation of a low-moisture, high-heating-value lump fuel using an inherently low-ash, low-sulfur LRC chemical cleaning would not be performed. This presumes that a low-cost oil can be found and that strong agglomerates can be produced at a low oil concentration. A complete chemical cleaning-oil-agglomeration scenario may be possible for producing a low-ash,

high-heating-value fuel for heat engine applications where the premium fuel value will be much higher than that of conventional steam coals.

Conclusions

- Tar oil is an effective LRC agglomerating oil at low-shear mixing conditions.
- Polar oils or solvents can be used to induce agglomeration when using tar-oil lights, a polymerized tar-oil fraction.
- Air-dried agglomerates containing tar-oil lights have significant resistance toward degradation and dust generation.
- The oil content of agglomerates can be reduced to between 3 and 5 wt% at thermal treatment temperatures of 260° and 230°C.
- Thermally treated agglomerates containing between 1 and 5 wt% of oil had insufficient strength toward degradation and dust generation.
- Thermally treated agglomerates are highly resistant to moisture reabsorption under immersion or high-humidity conditions.
- Coal adsorption can be used to significantly reduce the oil content of agglomeration process water.
- Carbon acid treatment at elevated pressures is effective for reducing the sodium content of LRCs.
- Selective agglomeration can achieve high coal yields and high ash reductions with specific LRCs.
- LRCs do not have to be chemically treated nor does the process water pH have to be adjusted to low values to achieve successful agglomeration.
- The EERC oil-agglomeration process economics are further hindered by the nature of the polar agglomerating oils as well as the high-heat load requirements for thermal treatment.
- The EERC coal cleaning-oil-agglomeration process is too costly to produce a low-ash, high-heating value fuel for the steam coal market when a coal cleaning step is incorporated.
- The EERC oil-agglomeration process has the potential for producing a high-heating-value lump fuel if a low-cost agglomerating oil can be identified.

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4.0 ADVANCED FUEL FORMS AND CO-PRODUCTS

Subtask 4.1 Beneficiation for Advanced Systems

APEC Energy Experts' Group Technical Seminar in Thailand

INTRODUCTION

At the request of the U.S. Department of Energy (DOE), Dr. Brian C. Young represented the Energy & Environmental Research Center (EERC) at the Asia-Pacific Economic Cooperation (APEC) Technical Seminar and Public Meeting on Clean Coal Technology in Chiang Mai and Bangkok, Thailand, over the week of September 6-10, 1993. The Technical Seminar and Public Meeting were organized in response to growing public, private, and government concerns associated with the increase use of lignite for power generation in Thailand. It was the first Technical Seminar of the APEC Experts' Group on Clean Coal Technology. The group was brought together for the exchange of information and constructive discussions on clean coal technologies for the power, industrial, and domestic sectors. Its overall goal was to assist in the implementation of the best available technology, at a price a country can afford, for improved efficiency and environmental performance in coal preparation and utilization.

The APEC Technical Seminar hosted some 60 delegates from 13 countries. Represented were Australia, Canada, China, Indonesia, Japan, Korea, Malaysia, the Philippines, Singapore, Sweden, Taiwan, Thailand, and the United States. On Monday, September 6, the delegates visited the Mae Moh lignite-fired power station. The delegates were first briefed about the facility, which has been operating since 1960. The power station has 11 units with a total capacity of 2025 MW. The units do not currently have flue gas desulfurization scrubbers, but plans are to install them on Units 10 and 11. Later in the day, the delegates visited the power station museum and viewed the deep, opencut lignite mine. The grounds surrounding the power plant and mine are attractive and impeccably kept. The Outlook Center has a traditional Thai open-structured building for viewing the mine, with a multitude of trees, colorful plants, and shrubs surrounding it.

On Tuesday, September 7, the chairperson, Mr. Peter Cover, panelists, and moderators met for a program briefing and a discussion on preparations for the Technical Seminar held on September 8 and 9 at Chiang Mai and the Public Seminar in Bangkok on September 10.

The Technical Seminar was divided into four panel sessions:

- Clean Coal Technologies Overview
- Coal Preparation
- Pollution Controls
- Solid-Waste Management

The paper from the EERC, "Upgrading of Low-Rank Coals for Conventional and Advanced Combustion Systems," coauthored by Brian C. Young, Mark A. Musich, and Michael L. Jones, was presented in the Coal Preparation session by Brian C. Young.

OBJECTIVES

- Prepare draft paper for APEC meeting in Thailand
- Present paper at APEC meeting
- Revise paper for APEC publication and complete report of APEC meeting

U.S. Technology: Perspective and Market Potential

Investments of US\$750 billion in new power plants for the Asia-Pacific region (excluding the U.S.) are projected for the period 1993–2010. Power production will increase from 550 GW in 1992 to 1350 GW in 2010. About half the total investments will be in coal-fired plants. Coal consumption will rise from 1.7 billion tons in 1993 to 2.8 billion tons in 2010. The large investment in coal-fired plants represents a significant opportunity for U.S. boiler and pollution control equipment manufacturers, as well as for consulting companies and institutions focusing on air, land, and water management and residue applications.

At the moment, sulfur dioxide (SO_2) is the major emission control priority for the Asia-Pacific countries. The next most important is ash collection and use or disposal. Nitrogen oxides and carbon dioxide emissions control are a low priority. Increasingly strict environmental legislation and enforcement procedures are directing coal-fired power plant executives to consider clean coal technologies for 95% recovery of SO_2 . Other options include fuel switching and improving the mix of energy sources, including the use of nuclear power. Since the cost of SO_2 postcombustion control is some 15% to 25% of the capital cost of a new pulverized coal-fired plant, alternative clean coal technologies such as circulating fluidized-bed combustion (CFBC), pressurized fluidized-bed combustion (PFBC), and integrated gasification combined cycle (IGCC) systems are also being considered. Some of the reported clean coal technologies are briefly noted below.

An advanced flue-gas desulfurization system offered by Pure Air (a joint venture between Air Products and Mitsubishi of North America) represents an alternative technology for the Asia-Pacific region. The company claims that, from experience with its demonstration plant at the Bailly (60 miles southeast of Chicago) 528-MW facility of North Indiana Public Service Company (NIPSCO), an advanced flue-gas desulfurization (AFGD) plant could be built and operated to meet SO_2 compliance codes at a cost of one-half that of conventional flue-gas desulfurization systems. At the Indiana plant, 90% to 97% of the SO_2 is removed. Using an innovative system, including a single absorber of up to 1000-MW capacity together with in situ oxidation to produce commercial-grade gypsum, this plant allows significant reduction in capital and operating costs. These costs are estimated to be US\$135–US\$150 per kW and 1–2 mills per kWh, respectively.

Another U.S. advanced pollution control system, offered for consideration by Babcock and Wilcox (B&W), is the SO_x – NO_x – RO_x –BOX™ (SNRB) process recently demonstrated with DOE support at a 5-MWe equivalent demonstration facility in Ohio Edison's R.E. Burger Plant. The demonstration attained consistent removal efficiencies of greater than 80% with the injection of commercially hydrated lime at calcium-to-sulfur stoichiometries of 1.8 to 2.0. Optimum removal was obtained at baghouse temperatures of 800° to 875°F. The use of modified lime hydrates or sodium bicarbonate yielded

improved performance, the latter material achieving greater than 90% SO₂ removal. The reduction of nitrogen oxides (NO_x) was consistently better than 90% at baghouse temperatures of 800° to 875°F. Particulate emissions were below New Source Performance Standards (NSPS) levels.

CFBC and PFBC systems are alternative technologies for dealing with sulfur in coal via in-bed capture. Foster Wheeler has had significant design, construction, and operating experience in the U.S. and Spain with CFBC units burning a variety of fuels, including tires, which have a high sulfur content. The 110-MW_e Nucla CFBC built by Ahlström Pyropower plant at Nucla, Colorado, a DOE demonstration plant, has shown that NO_x and SO₂ could be controlled below NSPS levels. The Tidd power plant, a 70-MW_e PFBC unit and a joint venture between Asia Brown Bovevi (ABB) and B&W, has been generating power since 1990. The facility has met its objectives of less than 0.51 lb/MMBtu of SO₂ (90% capture), 0.24 lb/MMBtu NO_x, and 0.02 lb/MMBtu particulates. The PFBC technology has been further demonstrated with 200-MW_{th} units in Sweden and Spain.

For countries planning to establish power plants by the turn of the century and beyond, IGCC technology promises higher thermal efficiency than advanced pulverized coal-fired or PFBC systems, along with enhanced emissions control by converting coal into a gas. Two-stage combustion of the coal is accomplished with a gasifier and turbine, partial oxidation of the coal occurring in the gasifier and complete combustion of the gas occurring in the turbine. Six IGCC demonstration projects are currently supported by DOE. The Duke Energy-DOE-sponsored IGCC project for Camden, New Jersey, proposes the construction of a 480-MW facility to demonstrate the British Gas/Lurgi (BGL) fixed-bed, slagging gasifier and a 2.5-MW molten carbonate fuel, all to be situated adjacent to the IGCC site. A high-sulfur coal will be burned to produce a clean, medium-Btu fuel gas. The project is expected to reach commercial operation in 1998. The current rapid developments in turbine technology will greatly enhance IGCC technology. The technology offers high efficiency and low SO₂ emissions; gypsum or fly ash disposal is not a problem; and CO₂ emissions are reduced by increased operating efficiencies.

The clean coal technology choices for the Asia-Pacific region are diverse and advanced in concept, offering high efficiencies and low emissions, but at a significant cost. U.S. power plant manufacturers and operations continue to develop a wealth of operating experience and performance data. In view of this background, such U.S. companies will have a competitive advantage to market and sell their various technologies to Asia-Pacific countries. This APEC meeting demonstrated the range of clean coal technology options and indicated their various stages of development and current utilization. Complementary and supplementary technology perspectives were also provided by representatives from Australia, Canada, China, Indonesia, Japan, Korea, Sweden, and Thailand.

The EERC has a role in providing assistance to assess the various clean coal technology options with respect to the fuel properties likely to be encountered in each country and the expected combustion performance, ash deposition, emissions, and disposal or reuse of solid residues. Although not on the APEC agenda at this meeting, the utilization of underground coal gasification (UCG), for which the EERC is committed to seek commercialization, is another clean coal technology option for certain countries in the Asia-Pacific region, e.g., Thailand, Indonesia, New Zealand, and Australia, where

deposits of low-rank coals are deep or inaccessible by conventional mining. EERC information on UCG was supplied to one of the Thai delegates keenly interested in this alternative clean coal technology.

Coal Preparation Session Overview

Conventional methods of coal preparation involving cleaning and upgrading are widely practiced in many countries to reduce mineral matter and inorganic sulfur content as well as to increase the energy content of coals. However, commercial cleaning is generally confined to high-rank coals.

Advanced technologies, including advanced froth flotation and selective agglomeration, are being applied to high-rank coals, but some processes are not yet economically practical and require further development and demonstration. The EERC has demonstrated that carbonic acid washing, as well as selective agglomeration, is technically effective to remove sodium and potassium for low-rank coals. Nonetheless, selective agglomeration is not commercially practiced yet because of the high cost of suitable binding oils.

A continuing focus of much research and development is the selection of drying technology for low-rank coals. Conventional thermal drying leads to stability problems in the dried coals, e.g., fines and dust generation, moisture reabsorption, and spontaneous heating (1). One process which appears to overcome these problems is high-pressure hot briquetting without a binder (2).

Another approach to producing dried low-rank coal is to convert the coal into a coal-water fuel that can be handled, transported, and stored like oil. Coal-water mixture technology has also been used to convert high-rank, low-ash coal and coal (high-ash) fines from coal preparation plants into boiler fuels. In the case of low-rank coal, hot-water drying (HWD) under pressure as developed by the EERC will irreversibly remove the moisture and seal the micropores of the coal with its condensed tars and oils (1, 3). Coal-water fuels, derived from HWD low-rank coals or from bituminous coals, have solid concentrations up to 60 and 70 wt%, respectively, and can be used as a replacement for fuel oil in a boiler or in gasification.

Pyrolysis, or mild gasification, of low-rank coals is an alternative upgrading technology for the production of a high-energy, low-moisture solid fuel, as well as liquid fuel products. Several processes are now being demonstrated on a large scale in the U.S. The upgrading process enables market entry for some coals, which, because of inferior quality, would otherwise be excluded.

Significant interest in coal briquetting exists in the Asia-Pacific region, with environmental benefits as the driving force. This technology enables the production of a clean-burning, low-moisture fuel from fine bituminous coals as well as from other coal types. Briquettes from coal, coal char, and coal biomass are available as a smokeless, convenient, and economical fuel for domestic and industrial use. Since some APEC economies depend heavily on firewood for home cooking and heating purposes, an urgent need exists to promote the use of domestic coal to preserve forests in the APEC region. These economies, including Thailand's, require expanded efforts to develop and demonstrate the technology.

The EERC paper, "Upgrading of Low-Rank Coals for Conventional and Advanced Combustion Systems," given by Dr. Brian C. Young was well received, and several questions were addressed. Particular interest was shown in the briquetting section of the paper. This interest in briquetting continued into the next day's session. Dr. Woo-Zin Choi (Korea) and Mr. Hiroshi Honda (Japan) discussed briquetting of coal and biomass. At the Korean Institute of Geology, Mining and Materials (KIGAM), Dr. Choi has been involved with Yontan briquetting and is now working on developing the briquetting technologies for Indonesian coal and sawdust using a starch binder. The briquettes are strong but not waterproof. Dr. Honda gave an account of the work done by Hokkaido Industrial Research Institute (HIRI) under Dr. T. Maruyama and the production of coal-biomass (bio-type) briquettes by a company in Hokkaido. Prior to joining the EERC, Dr. Young was developing coal-biomass (coal-biomass) briquette technology at CSIRO (Australia) and had visited the briquette plant referred to by Dr. Honda. Dr. Honda has yet to visit this plant.

The Coal Preparation session went very well, with good integration of the various papers. At the end of each day, the moderators were asked to summarize their sessions. Dr. Young and David Cain (Pacific Coal Proprietary Ltd.) assisted our Korean moderator, Dr. In-Chul Lee, in compiling the final summary of the Coal Preparation Session, which was presented at the Public Seminar on Friday, September 10, 1993.

Public Seminar

About 110 people in addition to the Technical Seminar delegates attended the Public Seminar. The Public Seminar was addressed by a panel consisting of representatives from DOE (Peter Cover), NEPO, and the East-West Center, as well as the Panel Session Chair. At this instructive meeting, after the Panel Session summaries were given the various questions requested from the public were generally directed toward the environmental impact of burning lignite coal. The question of using nuclear power was raised within this context. The cost of new clean coal technologies was also a recurring theme. The questions were addressed by the panel as well as delegates in the audience.

Conclusions

The opportunities for U.S. industry in the Asia-Pacific region for clean coal technologies are substantial. The large quantities of low-rank coal, some high in both sulfur and ash, particularly in Thailand, will require the use of effective control technologies and improved combustion systems, as well as advanced combustion systems, to meet increasing environmental and efficiency performance requirements being initiated now. The prospects for sales of demonstrated U.S. technologies, such as flue gas desulfurization equipment and CFBC systems, are very promising in the immediate future. In addition, the Asia-Pacific region offers admirable demonstration sites for operating the "new," i.e., advanced, technologies (PFBC, IGCC, and UGC) for the longer term. The significant operating experience and database on the new technologies from U.S. companies will be advantageous in expanding U.S. operations in the rapidly growing and energy-demanding Asian-Pacific markets.

Overall, the meetings were most challenging and rewarding, with a very positive interaction among the delegates. The Thai delegates were seeking specific answers to their many questions and concerns about the various clean coal technologies to assist

them in making decisions on the introduction of new coal-fired power plant technologies in the near future. The hosts for the meeting, the Electricity Generating Authority of Thailand (EGAT), the National Energy Policy Office (NEPO), and Ban-Pu Public Co., Ltd., were extremely hospitable, friendly, and attentive. The APEC meetings were well organized by Peter Cover, U.S. DOE Office of Fossil Energy, Washington, DC, and his staff.

The East-West Center, (Program on Resources: Energy and Minerals, USA) Honolulu, HI published the proceedings of the Technical Seminar in December 1993. The EERC paper was revised for this publication (5).

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4.0 ADVANCED FUEL FORMS AND COPRODUCTS

Subtask 4.2 Coproducts

INTRODUCTION

Besides a direct combustion fuel and a conversion (gasification and liquefaction) feedstock, coal is a valuable resource for producing non-fuel products. Conversion processes include coal gasification, which is a proven commercial technology both here (Dakota Gasification Plant at Beulah, ND) and abroad (Sassol, South Africa), and direct liquefaction, which has yet to be successful to the point of commercialization. Other conversion processes (e.g., pyrolysis) produce gas, liquid, and solid products and have the potential for supplying niche markets, making coal more valuable than merely as a heating fuel (1). Char markets include gas and liquid sorption applications for gas stream clean up and water purification, briquetted heating and cooking fuels, and formed coke as a replacement for, or supplement to, petroleum coke in the metallurgical industries. Pyrolysis liquids are used as heating fuel, feed for catalytic cracking to light gas for fuel use, chemical feedstock, beneficiation, and a binder for coal briquetting. Gas produced during pyrolysis generally has little value because of its low Btu content. It contains only minute amounts of small hydrocarbon gases (e.g., methane, C₂, C₃, and C₄ gases) along with moisture, carbon monoxide and carbon dioxide. The coproducts project was concerned with upgrading pyrolysis products from coal and evaluating them for specific applications.

OBJECTIVES

The overall objective of research on coproducts was to develop new process concepts for upgrading coal chars and liquids to meet product specifications applicable in the marketplace. The naturally high reactivity of LRCs, based on their surface area and oxygen content, has long been considered as providing a basis for producing activated carbons tailored to gas and water treatment applications, but the technical basis for realizing this potential is still lacking. The first objective was to conduct parametric tests on selected LRCs to assess activated carbon quality with respect to industry specifications for gaseous pollutant sorption and water treatment. Key issues examined included beneficiation, carbonization and activation conditions, aggregation, and densification techniques for imparting physical strength. The second objective was to conduct exploratory tests on techniques for improving the quality of primary coal liquids by in-process modifications starting in the freeboard of a bench-scale fluidized-bed carbonizer. These modifications were done to prevent polymerization reactions of volatile species and to promote controlled cracking in lighter products. Test conditions established a variable residence time in a fluid bed of dolomite or other material known to promote the cracking of coal tar.

ACCOMPLISHMENTS

Experimental

Feed Coal

An Alaskan (Beluga) subbituminous coal, a North Dakota (Beulah-Zap) lignite and a North Dakota leonardite were selected for evaluation as sources of char for use as adsorbent in gas stream and wastewater cleanup. One test, done with North Dakota lignite containing 10 wt% of polyvinyl alcohol (LigPVA), was meant to determine whether quality briquettes could be produced from the char. The coal was crushed, ground, and sieved in the usual manner to recover the -12- x +30-mesh fraction for use in the tests. The test coal was stored in plastic bags without headspace in covered 5-gallon pails. Results from thermogravimetric analysis (TGA) and proximate analyses are shown in Table 4.2-1.

Char Preparation and Testing

Char was prepared in milligram, gram and multigram batches of 20-40 mg, 5-10 grams, and 50-100 grams of raw coal in three reaction systems: the DuPont 2100/951 TGA, the so-called "large-scale" TGA built at the EERC, and an Integrated Bench-Scale Gasifier (IBG), respectively. The IBG is a fluidized-bed reactor in which the coal may serve as its own bed material, while the TGAs are fixed-bed units.

Shakedown of the IBG under pyrolysis conditions preceded char preparation experiments. During the shakedown, adjustments in operating procedures were made, and an operator's manual was written. Heatup rate was determined to be ~4°C/minute; the unit was pressurized to 150 psig and operated best with 50 - 80 grams of feed coal. The IBG was then used to prepare chars under a variety of test conditions for characterization and evaluation as a sorbent. The operating conditions, feed, and recovery are shown in Table 4.2-2.

TABLE 4.2-1

Thermogravimetric and Proximate Analyses Results of Feed Coals

Coal	As-received, wt%				Moisture-free, wt%			Moisture- and Ash-free, wt%	
	Moisture	Volatiles	Fixed C	Ash	Volatiles	Fixed C	Ash	Volatiles	Fixed C
Beulah Lignite	31.83	29.95	33.99	4.23	43.93	49.86	6.21	46.84	53.16
North Dakota Leonardite	25.03	38.73	28.54	7.70	51.66	38.07	10.27	57.58	42.43
Alaskan Beluga Subbituminous	21.63	36.44	36.29	5.60	46.50	46.31	7.15	50.08	49.87

TABLE 4.2-2

Pyrolysis Conditions and Char Yield

Sample	Atmosphere	Heatup	Feed, g	Recovery, g	Yield, wt%
Beulah Lignite					
Raw			N/A	N/A	
IBG030	N ₂	Slow to 850°C	52	11	40
IBG031	N ₂	Rapid at 850°C	50	16	61
IBG032	N ₂	To 500°C, then 850°C	52	16	59
IBG030-032	Primary Pot - Cleanout		154	20	25
IBG037	N ₂ , 20% Steam ¹	To 500°C, then 850°C	53	10	36
IBG038	N ₂ , 20% Steam ¹	Rapid at 850°C	54	10	36
IBG037-038	Primary Pot - Cleanout		107	12	21
IBG039	N ₂ , 20% Steam ¹	Slow to 850°C	50	2	8
IBG040	N ₂ , 20% Steam ¹	Rapid at 850°C	50	0	0
IBG0039-040	Primary Pot - Cleanout		100	41	78
IBG041	N ₂	To 500°C, then 850°C	53	10	36
IBG042	N ₂	Rapid at 850°C	54	13	47
IBG041-042	Primary Pot - Cleanout		107	21	37
IBG043	N ₂ /H ₂ O (5 Min)	To 500°C, then 850°C	59	9	30
IBG044	N ₂	Rapid at 850°C	53	13	48
IBG045	N ₂ /H ₂ O (5 Min)	Rapid at 850°C	53	2	7
IBG046	Ar/CO ₂ , cyl 75/25	To 500°C, then 850°C	57	17	55
IBG047	Ar/CO ₂ , cyl 75/25	Rapid at 850°C	55	12	41
Leonardite					
IBG073A	KOH, 20 psi, N ₂ , Steam ¹ (20 min)	850°C	64.7	17.9	28
IBG073B	N ₂ , Steam ¹ , (45 min)	850°C	59.3	15.2	26
IBG073C	N ₂ , Steam ¹ , (47 min)	850°C	59.3	16.5	28
IBG073D	N ₂ , Steam ¹ , (50 min)		100	26.7	27
IBG073E	N ₂ , Steam ² , (50 min)		100	22.2	22
IBG074A	N ₂ , Steam ¹ , (45 min)	850°	90	26.25	29
IBG074B	N ₂ , Steam ¹ , (45 min)		88.8	22.8	26
IBG076	N ₂ , 1 hr	700°C	76	27.7	37
IBG077	N ₂ , 1 hr	750°C	76.2	29.0	38
IBG078	N ₂ , 1 hr	750°C	77	27.8	36
IBG079	N ₂ , 1 hr	750°C	76.1	28.3	37
IBG080	N ₂ , 1 hr	700°C	79.0	29.5	37
IBG081	N ₂ , 1 hr	800°C	74.2	28.9	39
IBG080	N ₂ (30 min) 25% CO, 75% Ar (30 min)	750°C	67.9	21.0	31
IBG092	H ₂ O/N ₂ (30 min), N ₂ (30 min)	750°C	70.1	25.4	36
IBG093	23 psi, N ₂ Hold, 1 hr	500° - 750°C	54.4	24.4	45
IBG094	N ₂ + Steam, 1 hr	500° - 750°C	52.7	19.4	37
IBG095	N ₂ + CO/Argon	500° - 750°C	54.5	23.6	43
IBG096	N ₂ Hold, 1 hr	500° - 750°C	58.9	23.6	40
IBG104	N ₂ , 400°C, 30% H ₂ + 70% N ₂ , 1 hr	700°C	55.2	25.8	47
IBG105	N ₂ , 700°C, 30%H ₂ + 70%N ₂ , 1 hr	700°C	56.3	25.5	45

TABLE 4.2-2 (continued)

Sample	Atmosphere	Heatup	Feed, g	Recovery, g	Yield, wt%
IBG106	Cat. in Top, N ₂ 700°C, Cat. 30% H ₂ + 70%N ₂ , 1 hr	700°C	59.8	26.7	45
IBG107	Used cat., 30% H ₂ + 70% N ₂ , 1 hr	700°C	59.3	25.5	43
IBG108	50.0 g new cat. in top, 30% H ₂ + 70% N ₂	700°C	58	24.3	44
IBG109	Used cat., 22 psi, 30% H ₂ + 70% N ₂ , cat. 1/2 hr	700°C	56.8	26.8	47
Beluga Subbituminous					
IBG049	N ₂	Rapid at 850°C	61	21	84
IBG050	N ₂ , 20% Steam ¹	To 500°C, then 850°C	58	24	98
IBG051	N ₂ , 20% Steam ¹	Rapid at 850°C	59	21	85
IBG052	Ar/CO ₂ cyl 75/25	To 500°C, then 850°C	70	21	71
IBG053	Ar/CO ₂ cyl 75/25	Rapid at 850°C	57	18	77
IBG054	Ar/CO ₂ cyl 75/25	Slow to 850°C	60	20	81
IBG055	Ar/CO ₂ cyl 75/25	Rapid at 850°C (H ₂ O)	61	18	68
IBG056	Ar/CO ₂ cyl 75/25	To 500°C, St 5, then 850°C	58	18	73
IBG057	Ar/CO ₂ cyl 75/25	Rapid at 850°C (H ₂ O)	59	19	78
IBG058	N ₂ , H ₂ O 5%	Rapid at 910°C	51	7	33
IBG082	N ₂ , 1 hr	800°C	66.4	28.6	43
IBG083	N ₂ , 1 hr	750°C	68.3	29.4	43
IBG084	N ₂ , 1 hr	700°C	68.9	29.9	43
IBG085	N ₂ , 1 hr	750°C	71.9	28.1	39
IBG086	N ₂ , 1 hr	700°C	70.3	30.8	44
IBG087	N ₂ , 1 hr	800°C	68.1	29.3	43
IBG088	N ₂ , 1 hr	750°C	66.8	27.7	42
IBG089	N ₂ , (30 min), 25% CO, 75% Ar, 30 min	750°C	70.0	31.0	44
IBG091	H ₂ O/N ₂ (30 min), N ₂ (30 min)	750°C	65.7	22.6	34
TGA					
Lignite			88	46	52
Leonardite			86	39	45
Subbituminous			90	37	41

¹ Steam activation for 5 minutes.² Steam activation for 8 minutes.

During selected char preparations with the IBG, pyrolysis gas was monitored continuously with an on-line Fourier transform-infrared spectrometer (FT-IR), and samples were periodically collected in gas bags for later GC analysis.

The small TGA instrument was used for proximate analysis and to determine SO₂ adsorption-desorption of all chars prepared. The SO₂ adsorption-desorption values were used to compare char quality. A mixture of 5000-ppm SO₂ in argon introduced at the rate of 100 cm³/min provided the adsorbate. Sulfur dioxide-quality adsorption-desorption characterization of IBG030 to IBG040 chars was carried out at both ambient temperature and at 100°C. The remainder of the IBG chars were characterized at 100°C only. Desorption measurements were made at 100°C and at 400°C under flowing argon.

Char particles from lignite were aggregated into pellets using polyvinyl alcohol as a binder. These pellets were then tested for SO₂ sorption capacity and qualitatively for strength.

Catalyst Preparation and Testing

Preparation of nickel-substituted synthetic mica montmorillonite (NiSMM)

Nickel-substituted synthetic mica montmorillonite (NiSMM) was the catalyst used in testing catalytic cracking of tars resulting from char preparation from coal (2,3). The sample tested was prepared at EERC and evaluated both as a hydrogenation catalyst and a gasification catalyst. It was prepared as follows: A sodium silicate solution (27 wt% SiO₂) was prepared by dispersing 112 grams sodium silicate in 1200 mL deionized water. The sodium silicate solution was then exchanged three times with Amberlite IR 120-H cation resin. Next, 81 grams nickel acetate tetrahydrate was dissolved in 600 mL water and added with stirring to the silica dispersion. Then, 75 grams aluminum isopropylate and 2.4 grams ammonium fluoride were added with stirring. The resulting slurry was evaporated until the volume was about one third. Sixteen mL of aqueous ammonia (25% NH₃) was then added, and the slurry was transferred to a stainless steel liner. The liner was placed in a stainless steel pressure vessel without a stirring device. The temperature was slowly raised to 300°C and held at this level for 16 hours. The operating pressure was 1200 psi. The pressure vessel was then cooled to room temperature. The product was separated by centrifugation, washed with deionized water, and dried at 120°C for 16 hours. The dried material was ground to -48 mesh and calcined in air at 540°C for 6 hours. The calcined NiSMM material was stored in airtight bottles for further use.

The IBG was modified with a second stage for testing catalysts for use in tar cracking. The heated module was bolted to the top of the reactor and typically was maintained at a temperature approximately 100°C less than that of the reactor, i.e., typically 600°–630°C for a 700°C reactor. Approximately 50 grams of NiSMM tar-cracking catalyst was tested with this apparatus.

Column Chromatography of Selected Pyrolysis Tar

Six samples of pyrolysis tar were selected for analysis by open-column chromatography. Samples used were from IBG077, IBG085, IBG089, IBG090, IBG091 and IBG092 coal samples. Insufficient tar was collected from IBG077 and IBG085 to be analyzed by this method, so results were obtained only for the four remaining tars.

The appearance of the tars varied only slightly between the six samples. IBG 77 and 85 were dark colored water, appearing to have fine particulate matter in them. Samples 89 through 92 looked the same, except that they appeared to be much more oily and tarry than either IBG077 or IBG085. IBG89 had noticeably more tar and oil than the others.

Analysis Procedure

The pH of the tar sample was measured with pH paper. Extraction of the tar oils were attempted using dichloromethane as a solvent. The samples were dumped into a separatory funnel, and 50 mL dichloromethane was added. The funnel was shaken to mix

the solution, venting the funnel as it was shaken. The mixture was allowed to settle to allow phase separation and then the dichloromethane layer was drawn off. Extraction was repeated two more times for a total of three times, although the IBG 089 sample required 4 or 5 extractions because of the formation of an emulsion.

After the extraction, any solids (coal fines or ash) in the dichloromethane layer were collected using glass-fiber filter paper and rinsed with dichloromethane. The solids were weighed, and the weights were recorded. The water layer of the extraction was also filtered and solids weighed. All solids appeared to be coal fines.

The dichloromethane in the filtered extract was then stripped under partial vacuum, and the weight of the extract was recorded. Infrared spectra of the samples were obtained, and open-column chromatography was performed on the remaining sample to determine the fraction of aliphatics, large aliphatics, aromatics, and polar compounds.

Results and Discussion

Activated Carbon

The results of proximate analyses, listed in Table 4.2-3, show substantial differences in char product from the feedstock lignite used in Tests IBG030 to IBG047. Tests IBG039, 040, and 045 produced char from the lignite feed that was very high in ash as seen in Table 4.2-3. The recoveries of the lignite chars were all very low as compared with the char yield from the proximate analyses. Material from the primary pot made up some of the deficiency in recovery as seen from the proximate analyses of combined material from Tests IBG030, 031 and 032. Apparently as the coal is pyrolyzed, it decrepitates and blows over from the reactor to the traps, leaving an ash-enriched char to be collected.

At ambient temperature, SO₂ adsorption-desorption by the lignite char is excellent but falls off when the test is carried out at 100°C, as shown in Table 4.2-4. The experimental results in Table 4.2-4 show char-wt% SO₂ adsorbed at 100°C (from 5000 ppm in N₂) followed by char-wt% SO₂ desorbed, first under argon at 100°C, then at 400°C (carbon regeneration).

The temperature regime followed while preparing the lignite char has an effect on the activity. Staged heating, in which the coal is introduced into the reactor at 500°C and subsequently heated to 850°C, resulted in lignite char having higher SO₂ adsorption values than char prepared under slow or fast heatup. However, rapid heatup of the leonardite to 700°C or 750°C produced char that was more active than either the lignite or the subbituminous chars. Staged heating of the leonardite did not produce superior char over that of the rapid heatup but did enable the devolatilization of the feed to proceed with less charring of the tars.

On pyrolysis, the subbituminous coal results in much higher char recoveries than does the lignite coal, owing to the loss of more unpyrolyzed fines from the lignite. The subbituminous coal char produced under the same conditions (i.e., same mass of coal and same process) has SO₂ adsorption-desorption properties that are as good as those of the lignite char (Table 4.2-4). However, on a char-mass basis, the lignite char showed better adsorptive behavior. The fixed carbon and ash numbers are consistent with those expected from this coal.

TABLE 4.2-3

Proximate Analyses of Coals and Chars

	wt%			Moisture-free, wt%				Moisture- and Ash-free, wt%	
	Moisture	Volatiles	Fixed C	Ash	Volatiles	Fixed C	Ash	Volatiles	Fixed C
Beulah Lignite									
Raw	31.83	29.95	33.99	4.23	43.93	49.86	6.21	46.84	53.16
IBG030	1.93	7.27	77.69	13.11	7.41	79.22	13.37	8.55	91.45
IBG031	9.80	7.70	72.55	9.95	8.54	80.43	11.03	9.60	90.40
IBG032	4.76	6.95	74.33	13.93	7.30	78.04	14.63	8.55	91.41
IBG303132	38.26	15.42	35.77	10.54	24.98	57.94	17.07	30.12	69.86
IBG037	2.21	6.25	80.89	10.65	6.39	82.72	10.89	7.17	92.83
IBG038	1.56	6.52	78.47	13.45	6.63	79.71	13.66	7.67	92.32
IBG039	24.1	36.41	43.45	26.01	8.44	57.27	34.28	12.85	87.14
IBG040	16.99	11.83	51.61	19.57	14.25	62.17	23.58	18.65	81.35
IBG041	0.51	4.65	85.09	9.77	4.67	85.52	9.82	5.18	94.83
IBG042	6.43	6.03	78.30	9.24	6.45	83.68	9.87	7.15	92.85
IBG043	8.66	7.16	73.63	10.55	7.84	80.61	11.55	8.87	91.13
IBG044	6.99	8.72	74.93	9.36	9.38	80.56	10.06	10.42	89.58
IBG045	6.26	10.56	59.68	23.47	11.27	63.67	25.04	15.03	84.93
IBG046	0.74	4.77	83.31	11.19	4.81	83.93	11.27	5.42	94.59
IBG047	0.92	7.58	78.06	13.43	7.65	78.79	13.56	8.85	91.14
IBG048	1.02	3.50	81.95	13.53	3.54	82.80	13.67	4.10	95.91
Leonardite									
IBG076	15.60	9.97	54.49	19.89	11.81	64.56	23.57	15.45	84.47
IBG077	1.16	10.67	64.70	23.47	10.80	65.46	23.75	14.16	85.85
IBG078	2.53	10.96	62.04	24.47	11.24	63.65	25.11	15.01	84.99
IBG079	3.96	10.98	62.93	22.15	11.43	65.52	23.06	14.86	85.16
IBG080	4.47	11.69	51.93	31.91	12.24	54.36	33.40	18.37	81.62
IBG081	3.55	9.30	58.85	28.28	9.64	61.02	29.32	13.64	86.33
IBG082	9.57	5.38	73.23	11.79	5.95	80.98	13.04	6.85	93.12
IBG083	2.57	5.56	77.38	14.48	5.71	79.42	14.86	6.70	93.29
IBG084	2.01	8.69	76.01	13.30	8.86	77.57	13.57	10.26	89.76
IBG085	2.64	6.35	76.89	14.14	6.52	78.97	14.52	7.63	92.39
IBG086	1.67	7.39	76.28	14.67	7.52	77.57	14.92	8.84	91.18
IBG087	2.51	5.37	77.67	14.44	5.51	79.67	14.81	6.47	93.52
IBG088	2.79	7.04	74.04	16.10	7.57	79.61	17.31	8.42	88.51
IBG089	2.83	6.84	75.81	14.55	7.29	80.88	15.52	9.73	107.89
IBG090	2.43	11.94	61.27	24.36	12.03	61.73	24.54	13.56	69.57
IBG091	1.90	6.67	76.41	15.02	6.73	77.12	15.16	7.79	89.22
IBG092	1.48	11.09	61.51	25.92	11.20	62.15	26.19	12.98	71.99
IBG097	23.29	33.03	37.59	6.13	33.44	38.06	6.20	41.62	47.37
IBG098	9.94	22.70	57.44	9.91	22.96	58.10	10.03	27.75	70.23
IBG099	1.10	18.62	52.63	27.64	18.84	53.24	27.96	23.91	67.57
IBG100	1.48	18.72	54.26	25.54	19.11	55.38	26.07	23.00	66.67
IBG101F	17.72	36.46	41.04	7.78	36.85	41.48	7.86	42.99	48.39
IBG101P	3.17	31.68	39.31	25.83	32.02	39.73	26.11	37.36	46.35
IBG102P	2.16	26.78	44.99	26.07	27.38	46.01	26.66	32.35	54.35
IBG102M	1.70	22.84	41.04	34.43	23.25	41.77	35.04	27.07	48.64
IBG102CH	0.30	15.25	53.72	30.77	22.37	78.80	45.14	23.85	84.02
IBG103F	15.95	40.56	26.98	16.51	54.10	35.99	22.02	60.30	40.11
IBG103P	2.61	27.20	41.57	28.62	34.71	53.04	36.52	37.38	57.13

TABLE 4.2-3 (continued)

	wt%				Moisture-free, wt%			Moisture- and Ash-free, wt%	
	Moisture	Volatiles	Fixed C	Ash	Volatiles	Fixed C	Ash	Volatiles	Fixed C
IBG104	1.53	15.16	60.85	22.46	15.16	60.85	22.46	15.16	60.85
IBG105	1.19	15.01	61.58	22.29	15.01	61.58	22.29	15.01	61.58
IBG106	1.38	13.63	59.78	25.24	13.63	59.78	25.24	13.63	59.78
IBG107	4.65	12.43	60.58	25.33	12.43	60.58	25.33	12.43	60.58
IBG108	2.82	13.92	60.73	22.55	13.92	60.73	22.55	13.92	60.73
IBG109	2.28	11.50	62.49	23.77	11.50	62.49	23.77	11.50	62.49
Alaskan Subbituminous									
IBG049	0.98	3.82	79.52	15.68	3.86	80.31	15.84	4.58	95.42
IBG050	2.32	2.85	80.83	14.00	2.92	82.75	14.33	3.41	96.59
IBG051	1.00	5.00	80.49	13.53	5.05	81.30	13.67	5.84	94.17
IBG052	1.09	3.77	78.51	16.64	3.81	79.38	16.82	4.58	95.43
IBG053	1.23	4.76	74.63	19.41	4.82	75.56	19.65	5.99	94.04
IBG054	1.13	3.87	77.92	17.08	3.91	78.81	17.28	4.73	95.27
IBG055	1.15	4.48	73.42	20.96	4.53	74.28	21.20	5.75	94.26
IBG056	2.03	5.04	76.38	16.58	5.14	77.96	16.92	6.19	93.84
IBG057	1.06	4.51	80.29	14.14	4.56	81.15	14.29	5.32	94.68
IBG058	2.21	3.92	78.88	15.01	4.01	80.66	15.35	4.74	95.29
IBG059	1.75	3.60	80.78	13.87	3.63	82.22	14.12	4.26	95.74
TGALIG ¹	31.83	29.95	33.99	4.23	43.93	49.86	6.21	46.84	53.19
TGALEON ²	25.03	38.73	28.54	7.70	51.66	38.07	10.27	57.58	42.43
TGASUBB ³	21.63	36.44	32.29	5.60	46.50	46.31	7.15	50.08	49.87

¹ Beulah-Zap lignites.² Leonardite.³ Subbituminous.

The progress of pyrolysis in selected lignite char preparations was followed with FT-IR spectrometry. Examples of the resulting plots of CO and CH₄ infrared adsorption as a function of time are shown in Figures 4.2-1 and 4.2-2. The spectra show that staged heating (IBG037) results in higher production of methane and carbon monoxide from this lignite than either a rapid heatup (IBG038 and IBG040) at calcining temperature or a slow heatup (IBG039) from ambient to calcining temperature. Methane produced from cracking during rapid heatup and slow heatup was relatively constant, whereas a much larger quantity of methane results from staged heating. CO follows a similar trend. The beneficial effect of staged heating on char sorption has already been noted.

Adsorption-desorption values (denoted as TGALIG, TGALEON, TGASUBB) for SO₂ from the TGA of the three coals are included in Table 4.2-4. The lignite and subbituminous char values compare very favorably with the results obtained with the char produced in the IBG. Sulfur dioxide adsorption-desorption values for LigPVA char showed this char to be approximately the same as the coal char. However, 1.5-gram

TABLE 4.2-4

Weight Increase (wt%) Due to SO₂ Adsorption Followed by Weight Loss (wt%)
Due to Desorption

Sample	A Adsorp. (Ambient 5000-ppm SO ₂), wt%	B Desorp. (100°C, N ₂), Δ wt%	C Desorp. (100°- 400°C, N ₂), Δ wt%	A Adsorp. (100°C, 5000- ppm SO ₂), wt%	B Desorp. (100°C, N ₂), Δ wt%	C Desorp. (100- 400°C, N ₂), Δ wt%
Lignite						
IBG030	6.1	5.2	2.6	2.7	0.4	1.2
IBG031	-0.8	5.4	3.7	2.3	0.5	3.0
IBG032	0.7	3.7	3.0	1.4	1.1	-1.6
IBG303132		0	0		0	0
IBG037	7	5.4	2.0	2.5	0.5	1.7
IBG038	7.7	5.8	1.9	3.0	0.5	1.7
IBG039	5.4	4.4	3.8	2.0	0.3	3.5
IBG040	5.3	4.1	4.6	2.1	0.4	4.2
IBG041				1.8	0.2	1.4
IBG042				0.6	0.1	1.6
IBG043				1.0	0.2	1.7
IBG044				0.8	0.2	2.5
IBG045				3.2	0.5	2.5
IBG046				2.5	0.2	1.3
IBG047				2.8	0.5	1.7
IBG048				1.3	0.3	1.2
Leonardite						
IBG087				1.0	0.2	1.7
IBG088				1.4	0.3	1.9
IBG089				1.6	0.5	1.6
IBG090				2.8	0.5	1.6
IBG091				2.8	0.1	1.3
IBG092				3.0	0.4	1.3
IBG093				2.3	0.3	3.4
IBG094				2.7	0.4	2.2
IBG096				2.2	0.3	2.5
IBG104				2.0	0.5	2.6
IBG105				2.3	0.5	2.9
IBG106				2.56	0.5	3.1
IBG107				2.1	0.4	2.8
IBG108				2.1	0.4	3.1
IBG109				2.4	0.4	2.7
Subbituminous						
IBG049				2.1	0.4	1.5
IBG050				1.4	0.4	1.2

TABLE 4.2-4 (continued)

Sample	A Adsorp. (Ambient 5000-ppm SO ₂ , wt%	B Desorp. (100°C, N ₂), Δ wt%	C Desorp. (100°- 400°C, N ₂), Δ wt%	A Adsorp. (100°C, 5000- ppm SO ₂ , wt%	B Desorp. (100°C, N ₂), Δ wt%	C Desorp. (100- 400°C, N ₂), Δ wt%
IBG051				2.2	0.1	1.0
IBG052				2.1	0.6	1.0
IBG053				1.9	0.5	1.1
IBG054				2.0	0.5	1.1
IBG055				1.7	0.5	1.0
IBG056				2.5	0.6	1.3
IBG057				1.8	0.5	0.9
IBG058				1.6	0.5	1.7
IBG059				1.5	0.5	1.2
Various						
TGALIG				2.4	0.2	1.0
TGALEON				4.2	0.4	1.3
TGASUBB				1.9	0.4	0.9
LigPVA				2.1	0.6	2.1
Commercial Char ¹	4.4			0.7		
Unisorb				0.5	0.4	0.1
Berger Brothers 80-Activate				1.1	0.4	0.6
Berger Brothers 80 - Unactivated				0.5	0.3	0.4

¹ Coal char, -80x + 325-mesh

pellets prepared from the LigPVA char apparently had improved water resistance and hardness over those prepared from the char without additional binder, but no quantitative measures of hardness or water resistance were taken. Adsorption of SO₂ by a commercial char was lower at both ambient temperature and 100°C than the chars from coals selected for this project.

Char prepared from -12 x +30-mesh leonardite in the IBG are not easily compared with the lignite and subbituminous chars since leonardite decrepitated badly, resulting in reduced particle sizes and the concomitant increases in surface area. As a result, the particle sizes of the leonardite are smaller than those of the other two coals before and after charring. The higher surface area may be responsible for greater adsorption although, the lignite and subbituminous chars did not increase their adsorption capacity significantly when ground to approximately the same size as the leonardite.

Figure 4.2-1. Absorbance at 2173 cm^{-1} by the CO component of product gas from pyrolysis of lignite coal under staged (IBG037), rapid (IBG038) and slow (IBG039) heatup.

Figure 4.2-2 Absorbance at 3018 cm^{-1} by the CH_4 component of product gas from pyrolysis of lignite coal under staged (IBG037), rapid (IBG038), and slow (IBG039) heatup.

As noted from Table 4.2-4, the char, when prepared at 700°C, contains volatile material that is removed during the high-temperature desorption of SO₂. This loss in volatiles is probably due to partial oxidation of reactive carbon on exposing the char to air prior to use as sorbent. Upon heating the spent char to 400°C to desorb SO₂, loss of carbon oxides also occurs, resulting in the large loss in weight shown in the table.

Pyrolysis Cracking Products

Pyrolysis gases and liquids consist of carbon oxides that can be reduced to hydrocarbons and water, oils, and tars that contain large hydrocarbons, which can be cracked to produce smaller, gaseous hydrocarbons. The NiSMM evaluated as a cracking catalyst has the potential for accomplishing both. Figure 4.2-3 shows that CO is in product gas from five IBG tests with leonardite. The concentration of the gas is determined from the infrared absorbance at a selected frequency (2159 cm⁻¹) according to the Beer-Lambert law, $A = abc$, where A = absorbance, a = molar absorptivity, b = cell length, and c = concentration. The figure shows that the gas stream that has not been passed over hydrotreated NiSMM (IBG105 and IBG106) contained a higher concentration of CO than that passed over hydrotreated NiSMM (IBG107, IBG108 and IBG109). Figure 4.3-4 shows that methane is in the product gas. The gas stream in contact with hydrotreated NiSMM had a higher concentration of CH₄ than that which had not been in contact with a catalyst or in contact with a catalyst but without hydrotreatment. The infrared spectra obtained for the tests involving NiSMM display an absorbance band that has been tentatively identified as a metal carbonyl band, probably nickel carbonyl. These

Figure 4.2-3 Infrared absorbance of product gas, demonstrating the presence of CO.

Figure 4.2-4 Infrared absorbance of product gas, demonstrating the presence of CH₄.

spectra are undergoing further study to determine if this identification is accurate. If so, tests with this catalyst will be terminated and alternative catalyst materials will be evaluated.

The pH of the samples analyzed by column chromatography was the same for all four, i.e., pH = 8. The recoveries of IBG090 tar and IBG092 tar from the column were quantitative, as shown in Table 4.2-5. However, the recoveries of the other two tars were < 90%, indicating that some of the tar components were insoluble in any of the solvents. The unrecovered material was probably water that adhered to the silica gel and was not eluted by the organic solvents. The normalized wt% of alkanes plus branched alkanes was approximately 10 wt% for IBG090 and IBG092 tars compared with the 2 wt% and 6 wt% for IBG089 and IBG091, respectively. IBG089 and IBG090 tars contained at least 5% more aromatics than did the other two tars. IBG090 had the least and IBG091 had the greatest amount of polars, while the other two tars had essentially the same amount per unit weight.

Future Work

- A 60-day no-cost extension was requested to complete planned work that was unfinished because of unexpected reactor hardware problems. Mechanical difficulties, including burnout of a bank of heaters and failure of the pressure control valve, and unexpected problems with adapting a catalyst module to the reactor resulted in the inability to meet the original time line.

TABLE 4.2-5

Silica Gel Column Fractionation of Pyrolysis Liquids						
	IBG077 ¹	IBG085 ¹	IBG089	IBG090	IBG091	IBG092
pH	8	7	8	8	8	8
n-Alkanes, norm. wt%			1.7	3.8	1.7	2.1
Alkanes (Branched), norm. wt%			0.5	5.6	4.3	8.8
Aromatics, norm. wt%			37.4	35.9	27.0	29.2
Polars, norm. wt%			60.4	54.7	66.9	59.8
Total, norm. wt%			99.8	100.0	99.9	99.9
Recovery, %			88.6	100.4	86.6	101.9

¹ Insufficient Sample

- "Doped" char from coal containing added metal ions will be prepared and tested, and surface areas of selected char particles will be obtained.

Conclusions

- The amount of char product recovered from the reactor was greater when prepared from an Alaskan (Beluga) subbituminous coal than from a North Dakota (Beulah) lignite, because of loss of more fines from the lignite. Analysis showed that these fines were insufficiently pyrolyzed.
- Volatile matter in the subbituminous char product was typically lower than that in the lignite char.
- Staged heating during pyrolysis of the lignite coal resulted in more methane production than did slow or rapid heating.
- Sulfur dioxide adsorption as measured by TGA at 100°C by all three chars prepared in this project was as good as, or better than, that in commercial coal chars.
- Pellets prepared from lignite char and polyvinyl alcohol apparently showed improved water and apparent hardness.
- A module was designed as a secondary vessel to be attached to the top of the IBG reactor vessel. This vessel, which was heated by the reactor, contained a heated catalyst bed through which gases and tar vapors could pass for cracking and/or reduction.

- Char prepared from leonardite with rapid heatup to 700° and 750°C adsorbed more SO₂ than the lignite or subbituminous chars prepared at 850°C.
- The tars collected from the char production were typically composed of 90% aromatic and/or polar material.
- Hydrotreated NiSMM reduced CO concentration and increased CH₄ concentration in the gas stream.
- Hot hydrotreated NiSMM in contact with a gas stream containing CO may produce nickel carbonyl, a toxic gas.

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4.0 ADVANCED FUEL FORMS AND CO-PRODUCTS

Subtask 4.3 Low-Rank Coal Liquefaction

INTRODUCTION

Carbon monoxide and water have been utilized in the liquefaction of coal since 1921, when Fischer and Schrader demonstrated the effectiveness of this process (1). Improvements in the CO-steam process have increased conversions to soluble products, but extensive depolymerization and hydrogenation of the coal macromolecules require further catalytic hydrotreatment of the CO-steam product. The goal of the coal science team at the University of North Dakota (UND) Energy & Environmental Research Center (EERC) is the development of new homogeneous catalysts for the CO reaction. These catalysts are expected to aid in solubilization and preliminary reduction of low-rank coals (LRCs) to a high-quality intermediate product that can be easily catalytically converted to distillate fuels with low heteroatom content.

Catalysis of the first stage of coal liquefaction involves improving the rates of bond cleavage reactions leading to improved solubility and the rates of preliminary reduction or hydrogen transfer reactions so that oils and asphaltenes are produced without extensive retrogressive reactions. The catalysts should be able to interact effectively with the colloidal coal matter to generate soluble products at moderate temperatures. Thus various inexpensive and disposable inorganic agents that are soluble in the reaction vehicle are being investigated. Sodium aluminate catalyzed the solubilization of Australian coals in the CO/H₂O system and in water/hydrogen-donor solvent mixtures (2, 3). Previous work at the EERC demonstrated that aqueous sodium aluminate was also effective for Wyodak subbituminous coal (4). High conversions comparable to those obtained with hydrogen-donor solvents and hydrogen sulfide were obtained. In this report, the suitability of the intermediates from catalyzed and uncatalyzed CO/H₂O reactions are compared as a feed for catalytic hydrogenation.

OBJECTIVES

The efficient production of environmentally acceptable distillate fuels requires catalysts for hydrogenation and cleavage of the coal macromolecules 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. In the UND/EERC processes, CO/H₂O or CO-donor solvent systems are used in the first stage. 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 has been attributed to coke formation (5), metals deposition (6), and inhibition of the active center by chemisorbed compounds (7).

The objectives of this research project are to develop and test 1) novel homogeneous catalysts for first stage and 2) 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 macromolecules, but yet do not possess strong acidities that lead to coking at high temperatures.

ACCOMPLISHMENTS

Experimental

Preparation of Catalysts

An Amocat-IA cobalt-molybdenum catalyst was presulfided by heating with a small amount of sulfur and 1000 psi of hydrogen in a 15-mL rocking microreactor heated at 350°C for 3 hours. The clay-supported iron catalysts were obtained from Universal Fuel Development Associates and were sulfided in situ by adding a small amount of elemental sulfur with the catalyst prior to hydrotreating.

Preparation of Tetramethylammonium Aluminate

A solution of 1.92 g of aluminum nitrate nonahydrate in 50 mL of deionized water was placed in a 250-mL centrifugation flask. To this solution, 2 g of 30% ammonium hydroxide was added slowly with vigorous stirring. The white gel-like precipitate was separated by centrifugation, washed with deionized water, and resuspended in 10 mL of water. To this suspension, 2.6 g of tetramethylammonium hydroxide was added with stirring. Upon addition of tetramethylammonium hydroxide and stirring, the white precipitate dissolved to give a clear solution. Sufficient water was added to make 25 mL of solution. This solution of tetramethylammonium aluminate was stored for further use.

Preparation of Soluble Aluminosilicate

A solution of sodium silicate was prepared by dissolving 2.72 g of sodium silicate (27% SiO₂) in 50 mL of deionized water. The sodium silicate solution was ion-exchanged with Amberlite IR (120-H) resin until the pH was between 2 and 3. To this solution was added 4.6 g of tetramethylammonium hydroxide (20%). This solution was mixed with a solution of tetramethylammonium aluminate prepared as described above. The clear solution of soluble aluminosilicate was stored for further use.

Preparation of Magnetite and Maghemite

Magnetite was prepared by a procedure similar to that reported earlier (8). Dry nitrogen was bubbled through 560 mL of deionized water placed in a three-necked flask. Iron(II) sulfate heptahydrate (80 g) was added to the flask and stirred until the iron sulfate dissolved. The greenish-brown solution was stirred at 90°C under nitrogen for 30 minutes. A solution of 6.46 g of KNO₃ and 44.9 g KOH in 240 mL of deionized water was added dropwise to the flask. The black precipitate formed was stirred at 90°C for 60 minutes. The product was then cooled overnight. The black solid (Fe₃O₄) was separated by centrifugation, washed with deionized water, and subsequently vacuum-dried.

A 10-g portion of the magnetite (Fe_3O_4) was calcined in air at 250°C for 3 hours to give a rust-colored powder (maghemite, Fe_2O_3).

Preparation of Iron Oxoaluminate

Iron oxoaluminate tetraisopropoxide was prepared by a procedure similar to that reported earlier by Ouhadi and others (9). A 100-mL, three-necked flask was attached to a distillation assembly and baked under dry nitrogen to expel moisture. Aluminum isopropylate (2.04 g), iron(II) acetate (0.87 g), and tetralin (10 g) were introduced into the flask. The flask was heated in a stream of nitrogen. Upon heating, the iron acetate and aluminum isopropylate dissolved in tetralin to give a dark-green solution, and isopropyl acetate began to distill. The heating was continued until isopropyl acetate ceased to distill. The green solution was stored under nitrogen.

CO/ H_2O 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 (if needed) 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. The resulting slurry was acidified with dilute HCl. The desired amount of the internal standard was added to the product slurry, and the product slurry was extracted with methylene chloride. The methylene chloride extract was dried over molecular sieves (4 Å) and analyzed by gas chromatography with flame ionization detection (GC/FID) and gas chromatography/Fourier transform infrared spectrometry/mass spectrometry (GC/FT-IR/MS).

CO/ H_2O Liquefaction of Coals

A slurry consisting of 10.0 g of coal (as-received Wyodak-Clovis Point), 2.5 mmol of NaAlO_2 (if desired) dissolved in 6.0 g of water, and 10.0 g of tetralin (solvent) was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of carbon monoxide 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. The reactor was cooled to room temperature, and the gases were removed. The products were distilled to remove water. The remaining slurry was extracted with tetrahydrofuran (THF). The THF-insoluble product was dried under vacuum and weighed. The percent conversion was calculated on the basis of the coal (maf) that did not appear in the THF-insoluble fraction. The extract was evaporated to remove THF. The resulting low-severity products from sodium aluminate-catalyzed (SA-LSW) and uncatalyzed reactions (U-LSW) contained the original tetralin as well as the solubilized coal material. These were stored under nitrogen for further catalytic hydrotreating.

The composition of THF-soluble products was determined by adding an aliquot of this product to a large excess of heptane with vigorous stirring. The heptane-insoluble product was separated by centrifugation, washed with heptane, dried in vacuo at 50°C , and weighed. The heptane-soluble product was evaporated to remove heptane and kept for further analyses. The heptane-soluble yield was calculated with the following equation where % heptane solubles includes gas and water:

$$\% \text{ heptane solubles} = \% \text{ conversion} - \% \text{ heptane insolubles} \quad [\text{Eq. 4.3-1}]$$

Catalytic Hydrotreatment of Low-Severity Intermediates

A slurry consisting of 3 g of SA-LSW or U-LSW, 10 wt% of desired catalyst, and 2 wt% of sulfur (if needed) was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of hydrogen gas. The reactor was heated to 425°C in a rocking autoclave (initial heatup time = 15 minutes) and held at this temperature for 3 hours. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The product slurry was extracted with THF, and the THF-insoluble product was dried under vacuum and weighed. The THF-insoluble fraction was used to determine the amount of coke formed as a result of retrogressive reactions during hydrotreatment. The extract was diluted to 250 mL with THF. A 4-mL aliquot of the THF solubles was mixed with 1 mL of solution of internal standard (a mixture of 2,2,4-trimethylpentane and *n*-octadecane in dichloromethane) and analyzed by gas chromatography (GC). The remaining THF-soluble fraction was evaporated to remove THF, and the dark oil was added to a large excess of heptane and stirred. The heptane-insoluble product was separated by centrifugation, washed with heptane, and dried in vacuo at 50°C. The percent conversion was calculated on the basis of the heptane-insoluble product that was converted to heptane-soluble product (oils). The conversion and yield data are given in Table 4.3-1.

Instrumentation

Quantitative GC/FID analyses were performed with a Hewlett-Packard (HP) 5880A gas chromatograph equipped with a Petrocol capillary column. A mixture of isooctane and *n*-octadecane was the internal standard. GC/FT-IR/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 capillary column with a 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 point components.

Infrared spectra were obtained in KBr on either a Perkin-Elmer Model 283 spectrometer or a Nicolet 20SXB FT-IR spectrometer, equipped with a mercury cadmium telluride (MCT) detector, and a Nicolet 1280 computer with a fast Fourier transform coprocessor.

Results and Discussion

Catalytic Hydrotreatment of Low-Severity Liquefaction (LSW) Products

The advantage of using a solubilization stage in coal processing is that almost all of the inorganic material present in the coal can be eliminated prior to catalytic hydrogenation over a supported catalyst. Thus the calcium deactivation that has seriously affected catalytic liquefaction in the low-rank coals can be avoided. Aqueous solubilization reactions that utilize carbon monoxide as the reductant gas have been extensively investigated in this and other laboratories over many years (10–12). Basic catalysts have been employed to achieve higher conversions. The CO/H₂O reduction has

TABLE 4.3-1

Catalytic Hydrotreating¹ of Low-Severity Products
from CO/H₂O Liquefaction of Wyodak Coal

Low-Severity Product	Catalyst	Sulfur, %	Temp., °C	Heptane Insol., %	Conv. to Heptane Sol., %
U-LSW ²	---	---	---	0.49	---
U-LSW	None	None	425	0.36	26
U-LSW	APC-Fe ₃ ³	2	425	0.26	47
U-LSW	K-10/Fe ₃ ⁴	2	425	0.22	56
U-LSW	Co-Moly	2	425	0.16	67
SA-LSW ⁵	---	---	---	0.61	---
SA-LSW	None	None	425	0.48	24
SA-LSW	APC-Fe ₃ ³	2	425	0.23	62
SA-LSW	K-10/Fe ₃ ⁴	2	425	0.20	68
SA-LSW	Co-Moly	2	425	0.20	68

¹ Reaction time = 3 hours, H₂ = 1000 psi (cold), low-severity product weight = 3 g, catalyst weight = 0.3 g.

² SA-LSW = Sodium aluminate-catalyzed low-severity product.

³ Catalyst washed with ethanol prior to drying and calcination.

⁴ Triiron was supported on K-10 in ethanol.

⁵ U-LSW = Uncatalyzed low-severity product.

been shown to be superior to that of hydrogen for the first stage of liquefaction. A number of candidates for improving the conversion in CO/H₂O were reported by Jackson and others (2, 3). Aqueous sodium aluminate gave good conversions of brown coal to oils at temperatures of 350° to 400°C. The mechanism for sodium aluminate activation of carbon monoxide to produce an effective reducing intermediate is still under investigation.

Investigations of homogeneous catalysts for coal liquefaction at the EERC (4) verified that sodium aluminate is also effective in improving the CO/H₂O liquefaction of low-rank western U.S. coals. High conversions to THF solubles were obtained for the Wyodak subbituminous coal (89%). These were substantially higher than those obtained in a similar CO/H₂O reaction with no added sodium aluminate (78%). Conversion of the Wyodak to THF solubles in a CO/H₂O liquefaction experiment with sodium hydroxide catalyst was substantially lower (72%).

A mixed solvent containing an organic solvent with lower vapor pressure (tetralin) was also used for the CO/H₂O reaction. Solubilization reactions of the Wyodak coal were performed in a wt water/wt tetralin ratio of 0.6, both with and without sodium aluminate, at 400°C for 30 minutes with an initial cold CO pressure of 1000 psi. Compared with

water only, the operating pressure as well as conversions to THF-soluble products was significantly lower for the mixed solvent system. The sodium aluminate-catalyzed reaction gave 79% conversion to THF solubles, whereas the uncatalyzed reaction gave only 63% conversion. The lower yields for the mixed solvent in both catalyzed and uncatalyzed reactions may have resulted from the lower water concentration. The dependence of the conversions on the CO and water partial pressures was previously described (13). It should also be pointed out that the lower fluid density in the mixed solvent reactions may have resulted in lower conversion. Higher conversions can be obtained by longer reaction times or higher temperatures, but minimal processing severity was desired for generating the intermediates needed for this study.

The yield of heptane solubles from the sodium aluminate-catalyzed reaction (CO-water-tetralin system) was the same (30% heptane solubles) as that obtained in uncatalyzed reactions in the same system (31% heptane solubles). Since the conversions were higher, the heptane-insoluble fraction was larger for the sodium aluminate-catalyzed reactions; thus, the two products did not have the same composition with respect to the solubility fractions.

Development of an economical process for liquefaction of LRCs requires an evaluation of the suitability of the soluble CO-steam products as a feed for catalytic hydrogenation. The catalytic hydrogenation is required for depolymerization to a distillable product with higher hydrogen content and low heteroatom content. The evaluation of product quality was determined by carrying out hydrogenations with both a conventional supported cobalt-molybdenum catalyst as well as with two dispersed iron sulfide catalysts. In these tests, the THF-soluble, low-severity products from the sodium aluminate-catalyzed (SA-LSW) and the uncatalyzed CO/H₂O reactions (U-LSW) were catalytically hydrotreated with 10 wt% of the catalyst at 425°C for 3 hours in hydrogen (1000 psi cold). Since the compositions of the SA-LSW and U-LSW were not identical, the percent conversion was measured as the percentage of heptane insolubles converted to heptane solubles in the hydrogenation of each intermediate with each catalyst. The conversion data and product yields are given in Table 4.3-1.

The thermal (noncatalytic) hydrogenation of the SA-LSW product converted 24% of the heptane-insoluble fraction to heptane solubles. Thermal hydrogenation of the U-LSW product gave a similar conversion to heptane solubles (26%).

The supported cobalt-molybdenum catalyst was presulfided in hydrogen sulfide/hydrogen (10% H₂S). Hydrogenation of the SA-LSW with the presulfided cobalt-molybdenum sulfide catalyst resulted in a high conversion (68%) of the heptane-insoluble fraction to heptane solubles. Hydrogenation of the U-LSW with this catalyst also gave a high conversion to heptane solubles (67%).

In contrast to the molybdenum catalyst results described above, the results obtained with sulfided iron catalysts demonstrated significant differences for the hydrogenation of the low-severity products obtained from the sodium aluminate-catalyzed and the uncatalyzed reactions. An iron/alumina-pillared montmorillonite catalyst was sulfided in situ by adding elemental sulfur to the reactants. The hydrogenation of SA-LSW with this catalyst gave a 62% conversion to heptane solubles. A conversion of only 47% was obtained with the U-LSW product. The very large increase in conversion to heptane solubles in the SA-LSW experiment clearly demonstrated that the use of sodium

aluminate catalyst in the CO-water pretreatment solubilization stage had a beneficial effect on the quality of the low-severity product.

This improvement in the hydrotreatability of the low-severity product as a result of sodium aluminate catalysis was further demonstrated by a different sulfided iron catalyst. This catalyst was prepared by the impregnation of triiron complex on an acid-washed montmorillonite. The sulfidation was performed in situ with elemental sulfur, and reaction conditions were the same as before. The reaction with the SA-LSW gave an excellent conversion to heptane solubles (67%), which compared favorably with that produced by the molybdenum catalyst. As in the reactions with the pillared clay-supported iron sulfide catalyst, the reaction of this clay-supported iron catalyst gave a much lower conversion (56%) with the U-LSW.

CO/H₂O Reactions of Polynuclear Aromatic Hydrocarbons

Previous studies have shown sodium aluminate to be an effective catalyst for hydrogen transfer to linear polynuclear aromatics (14). Several more solid as well as soluble catalysts have been prepared and tested for the CO/H₂O hydrogenation of polynuclear aromatics. Anthracene and pyrene were used as test compounds to investigate the hydrogenation of polynuclear aromatic hydrocarbons by the aqueous CO system. The reactions were carried out by heating the substrate and catalyst in water at 400°C for 2 hours in the presence of 1000 psi of CO (initial cold pressure). Reaction conditions and conversion data are given in Table 4.3-2.

Reaction of anthracene with soluble aluminosilicate (tetramethylammonium salt) gave only 44% conversion of the substrate to hydroanthracenes. The product was mostly 9,10-dihydroanthracene plus a small amount of tetrahydroanthracene. Compared with sodium aluminate (82% conversion), soluble aluminosilicate showed considerably lower hydrogen-transfer activity.

Tetramethylammonium aluminate gave slightly higher conversion (83%) of anthracene than sodium aluminate. Product distribution was similar to that obtained with the sodium aluminate-catalyzed reduction of anthracene (14, 15). Thus the tetramethylammonium aluminate must function similarly to sodium aluminate, and the cation is probably not involved in the mechanism.

Reduction of anthracene in CO/H₂O was also investigated using an insoluble (solid) catalyst. Magnetite (nonsulfided) gave a significantly lower conversion (74%) than the sodium aluminate-catalyzed hydrogenation of anthracene. The major product was 9,10-dihydroanthracene, and a small amount of tetrahydroanthracene was also formed. The reaction of magnetite with pyrene gave a very poor conversion (2%), and dihydropyrene was the only product. These data are consistent with sodium aluminate-catalyzed CO/H₂O reduction of pyrene (15). Magnetite is a good catalyst for the water-gas shift reaction. It appears that whatever complex forms between magnetite and CO, it is unable to transfer either hydrogen or electrons to anthracene very effectively.

CO/H₂O Hydrotreatment of Coals

During our previous study of homogeneous catalysts for first-stage coal liquefaction, catalysts for improving the conversion and product quality of liquefactions carried out in

TABLE 4.3-2

Catalytic Hydrogenation of Polynuclear Aromatic Hydrocarbons¹

Catalyst (mmol/g substr)	Substrate (mmol)	Conv., %	Major Products (mmol)
SA (0.50)	Anthracene (2.80)	44	9,10-Dihydroanthracene (1.20) Tetrahydroanthracene (0.02)
TMAAlO ₂ (0.50)	Anthracene (2.86)	83	9,10-Dihydroanthracene (2.21) Tetrahydroanthracene (0.19)
Magnetite (0.50)	Anthracene (2.92)	74	9,10-Dihydroanthracene (2.04) Tetrahydroanthracene (0.12)
Magnetite (0.50)	Pyrene (2.47)	2	Dihydropyrene (0.04)

¹ Reaction temperature = 400°C, reaction time = 2 hours, reductant (CO) = 1000 psi.

aqueous systems were investigated. However, these reactions generated very high operating pressures. To reduce the operating pressures, a mixed solvent system consisting of 10 g of tetralin and 6 g of water was used. Since the first-stage liquefaction product is used as a feed for the subsequent catalytic hydrotreatment, tetralin was especially amenable because it gives a soluble first-stage product that can be directly used for the second-stage reaction. Furthermore, the product workup is also simplified. The reaction conditions and yield data are given in Table 4.3-3.

Previous results have shown that the addition of sodium aluminate to the CO/H₂O system improves the conversion of Wyodak subbituminous coal to distillate and soluble products at 400°C (14). Since high conversion rates to THF solubles are easily obtained at 400°C without any promoter or catalyst with the LRCs, the conversion to oils, asphaltenes, and distillate was accurately determined to evaluate the activity of sodium aluminate. The composition of the distillate, oil, and asphaltene product obtained after first-stage liquefaction in aqueous CO was determined for comparison with that obtained in organic solvents with CO or with hydrogen. These studies have indicated that the volatile first-stage product from aqueous liquefaction contained large amounts of phenolics rather than hydrocarbons, as is usually seen for organic solvent liquefaction. As a consequence, the distillate can be removed and used elsewhere, so that hydrogen is not wasted in deoxygenation of phenols.

Reaction of Wyodak coal was carried out by heating a well-mixed slurry of coal in aqueous sodium aluminate plus tetralin (a mixture of 10 g of as-received coal, 10 g of tetralin, 6 g of water, and 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 (73%) to THF-soluble products, with 37% heptane-insolubles and 36% heptane-solubles (oils). Similar reaction in the absence of sodium aluminate gave 63% conversion of the coal to THF-soluble products, with 32%

TABLE 4.3-3

Catalytic Liquefaction¹ of Wyodak Coal

Catalyst (mmol/g coal)	Coal, as-received (g)	Solvents (g)	Conv. ² , %	Products, %	
				Hept-I	Hept-S
None	Wyodak (10)	Tetralin (10) Water (6)	64	32	32
NaAlO ₂ (0.5)	Wyodak (10)	Tetralin (10) Water (6)	73	37	36
AS ³ (0.5)	Wyodak (5.0)	Tetralin (5) Water (3)	69	40	29
TMAAlO ₂ ⁴ (0.5)	Wyodak (10.0)	Tetralin (10) Water (6)	63	35	28
Magnetite (0.5)	Wyodak (5.0)	Tetralin (5) Water (3)	88	64	24

¹ Reaction temp. = 400°C, reaction time = 30 min, reductant gas (CO) = 1000 psi (at room temperature).

² Conversions are based on the amount of initial coal (maf). Heptane solubles are by difference, also includes water and gas.

³ AS = Soluble aluminosilicate.

⁴ TMAAlO₂ = Tetramethylammonium aluminate.

heptane-insoluble and 32% heptane-solubles (oils). These data indicate that sodium aluminate promotes the liquefaction of LRCs in aqueous as well as water-tetralin solvent systems.

Studies were also initiated to investigate other catalysts for aqueous CO liquefaction of coal. Reaction of Wyodak coal in the water-tetralin system was carried out using tetramethylammonium aluminate under reaction conditions identical to the sodium aluminate-catalyzed reaction. Tetramethylammonium aluminate gave a little lower conversion to THF-soluble products and lower conversion to heptane-soluble products, so it is probably inactive as a catalyst. The reaction of Wyodak coal was also carried out with soluble aluminosilicate in the water-tetralin solvent system under the above conditions. This catalyst also gave lower conversion (69%) to THF-soluble product than sodium aluminate, and the conversion to heptane solubles (oils) was significantly lower. These attempts to modify the catalyst structure were not successful.

The liquefaction of Wyodak was also carried out in tetralin-water using a high-surface-area solid catalyst (magnetite). This catalyst gave a very high conversion level (88%) to THF-soluble material. However, the conversion efficiency to heptane-soluble was only 24%. These data indicate that magnetite reacts differently than sodium aluminate, but no good explanation exists for this behavior.

The liquefaction product quality was determined by GC analyses of the oil fraction. Products in the oils were oxygenated compounds, such as methanol, 2-propanol (from acetone), and phenolics. In addition, hundreds of hydrocarbon components were present that are typically found in coal-derived products. Total phenolics amounted to about 5% of the starting maf coal. The ratio of tetralin to naphthalene was 25, indicating that approximately 4% of the tetralin was converted into naphthalene. A large number of alkyl tetralins and naphthalenes were also formed. Consequently, hydrogen transfer from tetralin also occurs during liquefaction. Based on the retention time of the components, it is concluded that sodium aluminate produced products with lower molecular weight than did the rest of the catalysts used in these investigations.

CO/H₂O Reduction of Anthracene

The second priority in our program was to understand the mechanism of the sodium aluminate catalysis. Sodium aluminate could probably activate CO for hydride reduction as well as sodium carbonate, perhaps even 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? To investigate the mechanism of NaAlO₂-catalyzed reduction of polynuclear aromatics in the CO/H₂O system, a series of reactions of a 1:1 mixture of anthracene and anthracene-*d*₁₀ was conducted. The reactions were carried out with and without catalyst at 400°C for 2 hours with 1000 psi of CO (initial pressure) to determine any differences in the isotope effects exhibited by the catalyzed reactions. Reactions of anthracene were also carried out with and without catalyst in D₂O for comparison with reactions carried out earlier in H₂O. Reaction conditions and analytical data are given in Table 4.3-4.

The results of the reactions of anthracene in D₂O exhibited a substantial decrease in conversion compared with those carried out in H₂O earlier in the project. The conversion of anthracene in the CO/H₂O system was 79% without NaAlO₂ catalyst and 82% with NaAlO₂. The lower conversions in D₂O (19% and 22% for uncatalyzed and catalyzed reactions, respectively) were expected for a reaction that formed hydrogen via a water-gas shift reaction followed by addition of hydrogen to anthracene. The results were consistent with the normal isotope effects observed in hydrogen addition reactions. Although inverse isotope effects were observed for the water-gas shift reaction that forms the hydrogen (16), the overall reduction in reaction rate for the CO-D₂O reactions was mainly determined by the normal isotope effect operating during the slower hydrogen addition step. A reaction involving donation of hydrogen from a formate intermediate to the anthracene might be expected to exhibit an inverse isotope effect similar to that found in the water-gas shift reaction, but we are not aware of any evidence that has established this effect as fact.

The conversion in D₂O was somewhat better with than that without the NaAlO₂ catalyst, as was the case with H₂O. A comparison of the magnitudes of the isotope effects do not allow us to reach a definitive conclusion about the catalytic mechanism.

A small inverse secondary isotope effect was observed for the reduction of anthracene compared with perdeuteroanthracene in the uncatalyzed CO/H₂O system. Furthermore, the NaAlO₂-catalyzed reaction showed an even greater inverse secondary isotope effect with respect to the aromatic substrate. These results were not expected.

TABLE 4.3-4

Reduction of Anthracene¹

Catalyst (mmol/g substr.)	Substrate (mmol)	Conv., %	Major Products (mmol)
None ²	Anthracene (2.87)	19	Dideutroanthracene (54) Tetradeutroanthracene trace
NaAlO ₂ ² (0.50)	Anthracene (2.86)	22	Dideutroanthracene (0.60) Tetradeutroanthracene trace
None	Anthracene (0.56)	20.5	Dihydroanthracene (0.11)
	Anthracene- <i>d</i> ₁₀ (0.53)	20.7	Dihydroanthracene- <i>d</i> ₁₀ (0.11)
NaAlO ₂ (0.50)	Anthracene (0.56)	22.2	Dihydroanthracene (0.12)
	Anthracene- <i>d</i> ₁₀ (0.53)	26.2	Dihydroanthracene- <i>d</i> ₁₀ (0.14)

¹ Reaction temp. = 400°C, reaction time = 2 hours, solvent (D₂O or H₂O) = 2 g, reductant (CO) = 1000 psi.

² D₂O solvent.

Since perdeuteroanthracene has a lower electron affinity (more negative reduction potential) than anthracene, one might expect a normal isotope effect for the reduction reaction, and previous results with various aromatics indicated that the electron affinity is a major factor in determining the reactivity of aromatics in the CO/H₂O system. The inverse isotope effect results indicated that the transition state involved in the reactions must occur later than it does in an electrode reduction. However, the observed results may have been caused by a reverse reaction of the dihydroanthracene products, which depletes the nondeuterated product with respect to the deuterated product via a primary isotope effect. Further work is needed to understand these results.

Catalysis of Hydrogen Transfer in LRC Liquefaction

Catalysis of the reactions of coals and model compounds in the CO/H₂O system has been explored. Sodium aluminate alone or in combination with iron was an effective catalyst for the first-stage reaction. The mechanism for this catalytic reduction is still unknown, but probably a formyl intermediate of some type was involved in the reaction.

An alternative to the CO/H₂O system for first-stage liquefaction is the CO-hydrogen donor solvent system. This system gave high rates of conversions to the THF-soluble intermediate, especially if hydrogen sulfide was used to promote the reaction. Unfortunately, sulfur was incorporated into the first-stage product. Are there inexpensive alternative homogeneous catalysts for the first-stage reaction in the CO-hydrogen donor systems? Specifically, could some species assist in the transfer of hydrogen from the donor solvent to the coal so as to give a more soluble product, more reduced product, or prevent retrograde reactions from occurring?

Further development of catalysts was pursued by investigating the reactions of an organic-soluble aluminate, which also contains iron. Catalysis of the reactions of coals

and model compounds in the CO-hydrogen donor systems focused on tetraisopropyl iron bis (oxoaluminate). This complex was easily prepared by heating aluminum isopropoxide with ferrous acetate in the reaction solvent (tetralin) until the isopropyl acetate coproduct was eliminated. Reactions of the iron oxoaluminate complex were carried out with anthracene and other probe compounds in tetralin solvent in a carbon monoxide or inert atmosphere (Table 4.3-5). Although the tetralin-soluble tetraisopropyl iron oxoaluminate was not expected to be stable at 400°C, a study of the catalytic activities of the colloidal or fine particle form generated during the thermal reaction was expected to lead to a better understanding of the role of the metals and the carbon monoxide in the reduction of coal.

The hydrogen transfer reaction of anthracene with tetralin in the absence of tetraisopropyl iron oxoaluminate converted a small amount (23%) to the hydrogenated anthracenes, 9,10-dihydroanthracene (DHA) and 1,2,3,4-tetrahydroanthracene (THA). A similar thermal reaction of anthracene with tetralin in a nitrogen atmosphere gave about the same yields of products (25%); thus CO has no effect on the reaction. The thermal reaction can be written as a radical chain reaction where hydrogen transfers between tetralyl radicals and anthracene (Equation 4.3-2) followed by hydrogen transfer between tetralin and the hydroanthracenyl radical (Equation 4.3-3). The reactor was freshly polished to remove any sulfide contamination, but it is possible that the steel walls of the reactor may have actually catalyzed the thermal reaction.

In the presence of tetraisopropyl iron oxoaluminate (TIOAL), the extent of anthracene reduction to DHA and THA increased substantially (35%) in the CO atmosphere. But in the TIOAL-catalyzed reaction under nitrogen, the conversion of anthracene was low (22%), as it also was in the uncatalyzed reaction. A reaction in air gave 18% conversion of anthracene. An additional experiment was conducted to demonstrate that the source of the hydrogens added to the anthracene was actually the tetralin and not the isopropyl groups originally attached to the iron oxoaluminate. The iron oxoaluminate was recovered from a thermal reaction at 400°C, washed with solvent, and oven-dried. A diffuse reflectance infrared spectrum of the solid indicated that no absorptions due to the alkyl groups were present. The anthracene/tetralin reaction with this material in CO gave a conversion (33%) similar to that obtained with the tetraisopropyl iron oxoaluminate.

Reactions were also carried out with aluminum isopropoxide and with ferrous acetate to determine the effect of materials containing only one of the oxymetal species, rather than the iron oxoaluminate structure. The conversions with aluminum isopropoxide and ferrous acetate were 24 and 28%, respectively, demonstrating the advantage of the combined form of these elements.

TABLE 4.3-5

Catalytic Activity of Tetraisopropyl Iron Oxoaluminate (TIOAL)¹

Catalyst (wt%)	Gas	Anthracene, mmol	Solvent (g)	Tetr./Naph Ratio	Conversion, %	Major Products (mmol)
None	CO	2.81	Tetralin (1.0)	22	23	DHA (0.57) THA (0.03)
None	N ₂	2.86	Tetralin (1.01)	20	25	DHA (0.61) THA (0.08)
TIOA1 (10)	CO	2.81	Tetralin (1.0)	17.2	35	DHA (0.78) THA (0.17)
TIOA1 (0.10)	N ₂	2.81	Tetralin (1.06)	29	22	DHA (0.57) THA (0.01)
TIOA1 (10)	air	2.75	Tetralin (1.0)	23.9	18	DHA (0.50)
IOA1 ²	CO	2.86	Tetralin (1.02)	19	33	DHA (0.85) THA (0.21)
AlPrO (0.20)	CO	2.86	Tetralin (1.09)	26	24	DHA (0.48) THA (0.02)
FeAc (0.20)	CO	2.81	Tetralin (1.0)	26	28	DHA (0.75) THA (0.07)
TIOA1 (0.10)	CO	2.81	Tetralin (1.09) Water (0.16)	25	43	DHA (1.08) THA (0.13)
TIOA1 (0.10)	CO	2.81	Tetralin (1.06)	29	22	DHA (0.57) THA (0.01)

¹ Reaction temp. = 400°C, reaction time = 2 hrs, CO or N₂ = 1000 psig.² Mixture of recovered iron oxoaluminate and tetralin.

Since hydrogen is transferred from the tetralin in these reactions, the mechanism here is not water-gas shift. Most likely the CO-activated iron oxoaluminate is an initiator for the radical chain reaction (Equation 1 and 2). The initiation could occur via hydrogen abstraction from tetralin or by electron transfer with the anthracene.

We hypothesized that the TIOAL could catalyze the water-gas shift reaction, if water were present in the reaction. This change in the role of the TIOAL was investigated by adding a small amount water (5%) to the reaction solvent. The amount of conversion for the 5% water reaction increased to 43%. Since the tetralin-to-naphthalene ratio was similar to that observed for other reactions described above, it is likely that hydrogen transfer from the naphthalene is occurring in this reaction along with the probable water-gas shift reaction.

The addition of isopropyl alcohol to the reaction (15%) was also investigated. This resulted in an additional conversion of anthracene. In this case the tetralin-to-naphthalene ratio increased substantially to 38; thus it appeared that the major hydrogen donor was the isopropyl alcohol, and a water-gas shift mechanism is likely to be a major factor.

The hydrogen transfer reactions involving iron oxoaluminate were further investigated with a second model system. Cleavage reactions of 1,3-diphenylpropane (DPP) were conducted in an alkane solvent (decane) at 400°C for 2 hours (Table 4.3-6). The thermal reaction of DPP in decane (CO atmosphere) occurred with the expected radical transfer/cleavage reaction to give mainly toluene and styrene in low conversion (18%). The thermal reaction is understood to occur by abstraction of a hydrogen atom from DPP and subsequent cleavage of the DPP radical to a benzyl radical (chain carrier) and styrene. The reactions are shown in Equations 4.3-4, 4.3-5 and 4.3-6. In addition, a small amount of styrene is reduced to ethylbenzene.

The addition of the TIOAL to the DPP-decane system resulted in a significant increase in the conversion of DPP. In the presence of CO, a 28% conversion of DPP was obtained, whereas in nitrogen the conversion efficiency was 24%. The reaction in CO gave much higher yields of all the cleavage products, including toluene, styrene, and ethylbenzene. The catalytic effect of the TIOAL could be attributed to the generation of radicals by the TIOAL that can initiate the chain as in Equation 4.3-4. A similar catalytic effect was described for hydrogen sulfide, pyrite, and pyrrhotite (17).

The solid iron-aluminum oxide recovered after thermal treatment of TIOAL in decane was tested with the DPP-decane system in CO. This material also gave an improved conversion of DPP (27%) with yields of toluene, ethylbenzene, and styrene similar to the TIOAL reaction.

The addition of anthracene to the DPP-decane system might be expected to produce an amplification of the DPP conversion by forming an effective chain-carrying radical. The addition of anthracene to the DPP-CO-decane system containing no TIOAL gave the same low conversion of DPP (18%), and no DHA formed. But in the presence of the TIOAL catalyst, the DPP conversion in the DPP-CO-anthracene-decane system increased to 54%. This increase was accompanied by a significant yield of DHA. When the reaction with TIOAL was run under nitrogen instead of CO, the conversion dropped back to 26%, and no DHA was found.

The increased levels of DPP conversion when anthracene is added can be explained by a model represented by Equation 4.3-5 and Equations 4.3-7 and 4.3-8 shown below. This model postulates initial formation of DHA or hydroanthracenyl radical and

TABLE 4.3-6

Reaction of Diphenylpropane¹

Catalyst (mmol/g substr)	Substrate, mmol	Solvent (g)	Gas (psig)	Conv., %	Products (mmol)
None	2.60	<i>n</i> -Decane (1.01)	CO (1000)	18	Toluene (0.36) Ethylbenzene (0.07) Styrene (0.21) Benzene (0.01) Indan (trace) Bibenzyl (0.1)
TIOA1 (0.10)	2.55	<i>n</i> -Decane (2.04)	CO (1000)	28	Toluene (0.67) Ethylbenzene (0.30) Styrene (0.18) Indan (0.01) Bibenzyl (0.01)
TIOA1 (0.10)	2.55	<i>n</i> -Decane (1.04)	none	24	Toluene (0.41) Ethylbenzene (0.08) Styrene (0.02)
Recov. IOA1 (0.10)	2.25	<i>n</i> -Decane (1.0)	CO (1000)	27	Toluene (0.66) Ethylbenzene (0.31) Styrene (0.15) Indan (0.01) Bibenzyl (0.02)
None	2.55	<i>n</i> -Decane (1.0) Anthracene, (90.10)	CO (1000)	18	Toluene (0.38) Ethylbenzene (0.09) Styrene (0.19) Anthracene (0.56)
TIOA1 (0.10)	2.55	<i>n</i> -Decane (1.0) Anthracene (0.1)	none	26	Toluene (0.49) Ethylbenzene (0.08) Styrene (0.14) Anthracene (0.62)

¹ Reaction temp. = 400°C, reaction time = 2 hours.

subsequent involvement of the hydroanthracenyl radical in the DPP chain decomposition. The rapid formation of dihydroanthracene with TIOAL is known from the work described above. Bockrath has shown that DHA is extremely reactive with benzyl radicals (18).

In conclusion, reactions of model compounds with the iron oxoaluminate catalyst showed that the TIOAL was able to initiate free radical reactions that transfer hydrogens between hydrogen-donor solvents and aromatics. Carbon monoxide was required for

activation of the catalytic sites that are responsible for this activity. In addition to catalysis of radical hydrogen transfer reactions, the iron oxoaluminate could effectively transfer hydrogen from water and alcohol to aromatics, presumably by a water-gas shift mechanism. This catalyst may be useful for first-stage coal liquefaction if it can effectively use carbon monoxide for reduction and promote cleavage reactions in the coal. In addition, the iron will eventually form a sulfide from the coal sulfur and form a useful hydrogen-activating site with a tiny domain size that can resist sintering because of the surrounding aluminum oxide structures.

Conclusions

The low-severity products from CO/H₂O reactions obtained with and without sodium aluminate were compared in hydrogenation tests with three catalysts as well as with the thermal noncatalytic reaction. The thermal reaction gave poor conversion efficiency to heptane solubles for both low-severity products. A significant difference in the conversions of the two low-severity products to heptane solubles was found for two clay-supported iron catalysts. The sodium aluminate-catalyzed CO/H₂O reaction gave a product with much higher potential for hydrotreating than that obtained from the uncatalyzed CO/H₂O reaction. In contrast, a commercial cobalt-molybdenum catalyst gave about 68% conversion for both low-severity products; thus the very effective hydrogen-activating molybdenum sulfide catalyst was able to compensate for the lower quality of the uncatalyzed reaction product. If the economics of coal liquefaction and catalyst recovery demands the use of the inexpensive and disposable iron catalysts, the use of sodium aluminate in a pretreatment solubilization step will be very important for increasing the yields obtained in the subsequent catalytic hydrogenation step.

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