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Coal Combustion Science Quarterly Progress Report January - March 1993

Principal Investigators:

Task 1. Coal Char Combustion ----- Robert H. Hurt
Task 2. Fate of Mineral Matter ----- Larry L. Baxter

Edited by Donald R. Hardesty

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Sandia National Laboratories
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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT

JANUARY-MARCH 1993

Submitted By: Donald R. Hardesty
Sandia National Laboratories, Livermore
Combustion Research Facility

Submitted To: Philip Goldberg
Pittsburgh Energy Technology Center

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MASTER

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L.L. Baxter and D. R. Hardesty

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT JANUARY — MARCH 1993

EXECUTIVE SUMMARY

Task 1: The Kinetics and Mechanisms of Pulverized Coal Char Combustion

In the Coal Combustion Laboratory this quarter, work focused on Subtasks 1.2 and 1.3. In Subtask 1.3, a new high-resolution captive-particle imaging technique was demonstrated on 100 - 200 μm char particles from Illinois #6 coal. The captive particle apparatus simulates the free-stream combustion environment while providing optical access for high-resolution video imaging of complete particle combustion lifetimes. The objective of this work is to obtain insights into the mechanisms of combustion, fragmentation, and final burnout, and to use the insights to aid in the interpretation of the quantitative data generated in Subtasks 1 and 2. The initial image sequences for Illinois #6 coal confirm the presence of an early near-extinction process (discussed in previous reports) and the asymptotic nature of the carbon burnout process. The technique also provides important new insights into the processes of particle fragmentation and reagglomeration at high burnout.

In Subtask 1.2 a set of highly-reacted Illinois #6 chars were characterized in detail in an attempt to explain the low reactivities previously observed at high conversion. The analytical techniques applied to the samples include: scanning electron microscopy, high-depth-of-field optical microscopy, coupled optical and scanning electron microscopy, coupled optical microscopy and laser spark spectroscopy, elemental analyses, FTIR spectroscopy, X-ray powder diffraction, and TGA. In this report, the results from these multiple complementary analyses are described and synthesized to shed new light on the process of char combustion during the latter stages of char burnout. The process of char combustion to complete burnout is interpreted in terms of the underlying physical and chemical phenomena responsible for the observed deactivation of the chars at high carbon conversions.

Task 2: The Fate of Mineral Matter

During this quarter, chemical fractionation tests on coals pulverized to different sizes were completed. These data will help us to assess the accuracy of the fuels characterizations for the purpose of interpreting inorganic release during coal devolatilization. Chemical fractionation tests on mineral species are proceeding for the same purposes, but these are not yet completed. A complete report on both the chemical fractionation procedure and the release of inorganic material during coal devolatilization will be issued when the remainder of the tests are complete.

On our second subtask, all fragmentation data have been collected. The data indicate, as in the past, that the amount of fragmentation of char particles is small compared to some previous reports. These results are confirmed by recent captive particle imaging (see Task 1 discussion in

this quarterly report) of char particles during combustion, in which no fragmentation has been observed. Fragmentation during devolatilization is still under investigation (data are all collected but analysis is not complete). These will be reported in the future.

Finally, considerable progress was made on the third subtask, in which we are developing spectroscopic techniques to determine the composition of inorganic phases within ash deposits. Combustion tests of an eastern, western, and blend of coals from Northern Indiana Public Services Co. (NIPSCO) were completed this quarter. Additional western coals from Northern States Power (NSP) are under preparation for combustion tests. In both cases, the coals represent interesting and relevant fuels for Combustion 2000 equipment. In the case of the NSP coals, the fuels are reported to have very similar elemental compositions but to exhibit markedly different deposition behavior in a combustor. The FTIR analysis technique shows promise of uncovering the differences in their ash deposition behavior. These tests are designed primarily to further develop the FTIR spectroscopic technique. Issues that have been investigated this quarter include the effect of changing surface temperatures, the effect of probe emissive properties, and the effect of gas phase emission on the measured surface emission spectra.

Several analyses have also been initiated on samples of ash deposits from the three NIPSCO coals. These include diffuse reflectance FTIR analyses, atomic emission elemental analyses, x-ray diffraction analyses, and SEM/XRD analyses. These should be completed early in the next quarter and will be compared to each other and with the *in situ* FTIR results to validate the latter. Several improvements in both experimental technique and data analysis have been completed or are in progress. These include modifying laboratory equipment in the area surrounding the deposition probe to minimize secondary reflections on the bottom of the probe, establishing blackbody reference spectra, pyrometrically measuring surface temperature, improving optical alignment, and improving our analysis of the gas-phase data. The focus of this report is on the last issue, with considerable detail included to describe how the *in situ*, real-time spectra of ash deposits in the pilot-scale MFC combustor are analyzed to remove the influence of the gas phase emission. Infrared-active gas-phase species such as water and carbon dioxide are the primary contributors to the interference in the spectrometer. Detailed determination of the chemical composition of surface species requires removing or, as a minimum, distinguishing spectral features that are attributable to the gas from those of the condensed-phase deposit. The data analysis technique is first discussed using idealized spectra and then demonstrated with actual data.

Future Work

On the char combustion task, during the next quarter work next quarter will focus on characterizing the changes in carbon structure that occur during char combustion. The primary objective is to identify the mechanism leading to deactivation and early near-extinction. The information on carbon structure will be combined with the information presented in the current report on particle morphology and carbon/mineral interactions to develop a complete description of the char combustion process to complete conversion. The captive particle imaging technique will be further developed and applied to several coals of varying rank.

On the mineral matter task, work in the next quarter will focus on analysis of fragmentation and inorganic release of material from coal for the entire suite of coals studied in the MFC. Continued development of our spectroscopic techniques for analysis of FTIR surface emission spectra will also be done. Final versions of future program plans will also be completed and submitted to PETC for review and approval.

PROJECT TITLE: COAL COMBUSTION SCIENCE

TASK 1: KINETICS AND MECHANISMS OF COAL CHAR COMBUSTION AND CARBON BURNOUT

ORGANIZATION: Sandia National Laboratories, Livermore

CONTRACT: FWP 0709

REPORTING PERIOD: January 1 - March 31, 1993

REPORTED BY: R.H. Hurt, K.A. Davis, N.Y.C. Yang, and D.R. Hardesty

Phone: (510) 294-3707 and (510) 294-2321

OBJECTIVE FOR TASK 1

The amount of unburned carbon in fly ash is an important concern in the design and operation of pulverized coal fired boilers, affecting combustion efficiency, boiler performance, and ash marketability. Carbon burnout is an especially important issue for low NO_x combustion systems. The objective of this task is to characterize the kinetics and mechanisms of char combustion and carbon burnout for strategic U.S. coals under conditions relevant to commercial pulverized coal-fired furnaces. In Sandia's Coal Combustion Laboratory (CCL), optical techniques are used to obtain high-resolution images of individual burning coal char particles and to measure, *in situ*, their temperatures, sizes, and velocities. Detailed models of combustion transport processes are then used to determine kinetic parameters describing the combustion behavior as a function of coal type and gaseous environment. Partially reacted char samples are also extracted and characterized with advanced solid-phase analytical techniques to understand the critical physical and chemical transformations that influence reaction rates and burnout times. The ultimate goal of the task is the development of coal-general models and correlations that predict the combustion rates and burnout times of chars over a wide range of conditions. These predictive techniques will be applicable both to current pulverized coal fired boilers and to advanced systems such as those being developed under the DOE combustion 2000 program.

Research is divided into the four subtasks described below, in accordance with the FY92 - FY94 project plan.

SUBTASK 1.1 KINETICS OF HETEROGENEOUS FUEL PARTICLE POPULATIONS

The objective of this subtask is to develop quantitative descriptions of single-particle combustion behavior and to identify their implications for global rates and for the performance of combustion systems. Experiments in the CCL provide a wealth of unique information on the combustion behavior of single particles as distinguished from macroscopic samples. Kinetic expressions based

on population statistics will be developed that more accurately describe the char combustion process as it proceeds into the important region of high carbon conversion. One-dimensional combustion models will be applied to char particle populations, exhibiting realistic heterogeneity in size and reactivity, to identify the important mechanisms leading to unburned carbon in fly ash.

SUBTASK 1.2 CHAR COMBUSTION KINETICS TO HIGH CARBON CONVERSION

The amount of unburned carbon in fly ash is an important concern in the design and operation of pulverized coal fired boilers. High carbon content represents a loss of efficiency, and prevents the sale of the fly ash byproduct as a raw material for the cement or construction industries. The objective of this subtask is to determine char oxidation kinetics valid to high carbon conversion (> 99%) and to identify and understand the mechanisms determining unburned carbon levels in fly ash from pulverized coal combustion. Fly ash samples will be generated under carefully controlled laboratory conditions, and the mode of occurrence and properties of the residual carbon will be characterized. The high-temperature combustion reactivity of the residual carbon will be measured and carbon transformations occurring during the combustion process will be characterized. The ultimate goal of the subtask is the development and validation of an advanced char oxidation model for accurate prediction of residual carbon levels.

SUBTASK 1.3 THE ROLE OF PARTICLE STRUCTURE AND THE CHAR FORMATION PROCESS IN COMBUSTION.

In this task, a high-resolution captive-particle imaging technique is being developed and applied to track morphological changes in individual pulverized coal particles during combustion. The images yield insights into the mechanisms of combustion and final burnout, which can be used to interpret the quantitative data generated in subtasks 1.1 and 1.2.

SUBTASK 1.4 UNIFICATION OF SANDIA CHAR COMBUSTION DATA BASE

The objective of this subtask is to complete the documentation of the existing Sandia data base, and to develop therefrom correlations and models allowing prediction of char reactivity and properties under technologically relevant conditions as a function of temperature, oxygen pressure, and coal rank and type. An additional objective is a unified treatment of nitrogen release kinetics during coal combustion.

SUMMARY OF TECHNICAL PROGRESS THIS QUARTER

Work this quarter focused on subtasks 1.2 and 1.3. In subtask 1.3, a new high-resolution captive-particle imaging technique was demonstrated on 100 - 200 μm char particles from Illinois #6 coal. The captive particle apparatus simulates the free-stream combustion environment while providing optical access for high-resolution video imaging of complete particle combustion lifetimes. The objective of this work is to obtain insights into the mechanisms of combustion, extinction, and final burnout, and to use the insights to aid in the interpretation of the quantitative data generated in subtasks 1 and 2. The initial image sequences for Illinois #6 coal confirm the presence of an early near-extinction process (discussed in previous reports) and the asymptotic nature of the carbon

burnout process. The technique also provides important new insights into the processes of particle fragmentation and reagglomeration at high burnout.

In subtask 1.2, an experiment was performed to determine the effect of sample capture and reinjection on single-particle optical measurements such as those presented in the previous quarterly report. Also for subtask 1.2, a set of highly-reacted Illinois #6 chars were prepared and characterized by a variety of analytical techniques in an attempt to explain the low reactivities previously observed at high conversion (Hurt and Hardesty, 1992). This work is reported in detail below.

SUBTASK 1.2 CHAR COMBUSTION KINETICS TO HIGH CARBON CONVERSION

Assessment of the Reinjection Technique

The previous report (Hurt and Hardesty, 1992b), presents optical data on partially-reacted Illinois #6 chars prepared by subjecting the samples to multiple passes through the CCL entrained flow reactor. In this section, capture and reinjection will be shown to have no significant effect on the fundamental combustion kinetics of individual particles. Fig. 1.1 shows *in situ* optical measurements of particle size and temperature for Pocahontas #3 coal, before and after capture and reinjection. The char particles in Fig. 1.1a were made by injection of raw coal in the 6 mole-% oxygen environment, and the optical data taken after 95 msec residence time. The char particles in Fig. 1.1b were generated by raw coal injection in the 6 mole-% oxygen environment, rapid quenching and collection after 47 msec residence time, and reinjection of the char in the 6 mole-% oxygen environment. The optical data for the reinjected char were taken after 95 msec residence time for direct comparison with the char formed *in situ*.

The optical data are essentially identical, with the breadth, shape, and detailed features of the particle temperature distributions unaltered by capture and reinjection. Single particle temperatures and burning rates are therefore not affected when the reaction is temporarily interrupted by sample capture. This result was expected, as chars are refractory solid materials (formed here at peak temperatures of 1600 - 1800 K) whose chemistry and structure should not be affected by rapid cooling, followed by exposure to the ambient air and rapid reheating to reaction temperature. It is important to note that at shorter residence times (less than about 50 msec) coals and reinjected chars will behave differently due to differences in heating and ignition mechanisms. The kinetic technique used in these and earlier studies, however, is based on optical measurements made at longer residence times where particle temperatures have equilibrated to values that are dependent on char reactivity and properties alone. A previous analysis of extinction phenomena (Hurt and Hardesty, 1992) has shown that multiple steady states are not expected for zone II char oxidation in the CCL, and thus particle temperatures will be independent of heating and ignition paths after the initial transient period.

In summary, both experimental and theoretical evidence indicates that capture and reinjection do not affect the temperatures and burning rates of individual particles after an initial transient heating zone. The possibility must be acknowledged, however, that the particle size distribution can be affected by sampling-induced fragmentation and/or reagglomeration. Fragmentation does not

Figure 1.1 Optical measurements of particle diameter and temperature during combustion of Pocahontas #3 coal and char. Oxygen concentration is 6 mole-%; gas temperature is 1555 K.

affect the fundamental kinetics determined from optical measurements (because particle size is measured *in situ*), but could affect the mass loss profiles determined by extractive sampling and tracer analysis. Low reactivities at high conversion have been observed in several independent experiments (see the next section) — the basic trend is well established and does not require confirmation from reinjection experiments. Nevertheless, accurate mass loss profiles at high conversion will be needed for the development of new kinetic models valid to very high extents of carbon conversion. To obtain these accurate mass loss profiles, a new hot-walled entrained flow reactor is being designed to allow for longer residence times in a single pass.

Characterization of Partially-Reacted Samples

In this section, a variety of analytical techniques are applied to a set of partially-reacted Illinois #6 char samples to begin to identify the underlying physical and chemical phenomena responsible for low reactivities at high conversion. These phenomena can be classified into three groups, related to: 1) particle morphology and its effect on surface area accessibility; 2) interactions between the carbon and the inorganic material; and 3) carbon structural changes on the atomic scale leading to the loss of available reaction sites. This report addresses the first two factors, while the third factor, carbon structural changes, will be addressed in the next quarterly report.

The set of partially reacted Illinois #6 char samples were obtained by extraction of samples from the CCL laminar flow reactor at residence times of 47, 72, 95, 117, 234, 351, and 468 msec. Residence times longer than 117 msec were obtained by sample capture and reinjection. Bulk carbon conversions were determined using total ash as a tracer. The end of devolatilization and the onset of heterogeneous oxidation are observed to occur at a reactor location that corresponds to approximately 47 msec of residence time. The weight loss measured at 47 msec is therefore used to approximate the high temperature volatile loss and then to compute conversions on a volatile-matter-free, or char, basis. No attempt is made here to interpret the relationship between carbon conversion and time, as it may be influenced by sampling-induced fragmentation and reagglomeration, as stated above.

Analytical Techniques

This section briefly introduces the various techniques used to characterize the samples of partially-reacted Illinois #6 chars collected at various residence times in the CCL flow reactor. Most of the techniques were applied on site at Sandia, California; exceptions are bulk elemental analyses (performed by Coors Analytical Laboratory, Golden, CO) and thermogravimetric analyses (performed by Professor Jon Gibbins' group in the Department of Mechanical Engineering, Imperial College, London).

Scanning electron microscopy

Scanning Electron Microscopy (SEM) was conducted using facilities at Sandia, California. The morphology of numerous individual particles was observed using both backscattered and secondary electron detection and local elemental composition was determined for selected particles by Energy-Dispersive X-Ray Spectroscopy (EDS). These results provide insight into the mode of occurrence of residual carbon and its relation to the inorganic material.

High depth-of-field optical microscopy

Partially reacted char samples were examined and photographed through a long focal-length microscope (model K2 from Infinity Photo-Optical), operating at a nominal magnification of 100x. The samples were examined on a diffuse, white background mounted perpendicular to the microscope axis, and the aperture was adjusted to achieve the depth-of-field necessary to bring groups of particles into simultaneous focus. Illumination was provided by a halogen lamp with two fiber-optic outputs equipped with spot lenses. Photographs were obtained through the microscope side port with a 35 mm camera (Nikon model F3) and enlarged to 8x10 or 11x14 formats.

Coupled optical and scanning electron microscopy

In order to relate features observed in optical micrographs to particle composition, a special mounting technique was developed to allow both optical and electron microscopy to be applied to single particles of interest. A small group of particles is scattered onto a copper grid and covered by copper tape with etch marks on its perimeter that provide points of reference for locating specific particles. No carbon-containing adhesives or coatings were used and copper was chosen as a substrate because it is not a species of interest in these experiments. Optical micrographs were first obtained as color prints then specific particles of interest were located by examining low magnification SEM images. High magnification images were then acquired and particle compositions measured by EDS.

Coupled optical microscopy and laser spark spectroscopy

In collaboration with David Ottesen at Sandia, California, Laser Spark Spectroscopy (LASS) was directly coupled to the long focal-length optical microscope and used to simultaneously acquire images and relative elemental composition information for individual char and ash particles from Illinois #6 coal. This technique gives similar information to coupled optical and electron microscopy (discussed above), but gives better information on bulk particle chemistry (as opposed to surface chemistry) than EDS. Spark spectroscopy does not, however, allow precise analysis of sub-particle regions.

Individual char or ash particles were selected, placed on a boron nitride substrate, photographed, and then immediately subjected to a high-energy laser pulse for LASS analysis. LASS uses a high-energy pulsed Nd:YAG laser to rapidly heat a target material which leads to the formation of an ionized plasma. This plasma produces atomic emission from the material, which can be examined using a time-gated diode-array detector and subsequently analyzed to determine the constituent elements of the original material (Ottesen et al., 1989). Since the spectral resolution is inversely related to the wavelength range being studied, the data presented herein are limited to wavelengths between 238 nm and 278 nm. This region was selected to include the intense carbon line at 247.9 nm and several intense lines of most of the abundant elements in coal ash. It was not possible, however, to select a spectral window wide enough to include strong calcium lines, while maintaining the resolution required to distinguish iron from carbon in the spectra. Since the laser spot size is a few times larger than most of the particles, vaporization of a portion of the

substrate is unavoidable and the use of this technique for small particles requires a substrate material that does not contain any of the elements of interest. Again, as with the SEM, adhesives must be avoided because of their carbon content; however, the use of a conductor, e.g. copper, is unnecessary. Boron nitride presents an excellent optical background for the high depth-of-field imaging and serves as a suitable substrate material as well. The spectra shown have been corrected for the two boron peaks which occur at 249.7 nm and 249.8 nm using a pure boron nitride spectrum taken from the same material used for the substrate with the same experimental system.

Under certain conditions these line intensities can be used to quantitatively determine sample composition using National Bureau of Standards tables of line intensities. However, because of incomplete particle vaporization, the dependence of line intensity on plasma temperature, and preferential vaporization of the more volatile species, the composition ratios reported here are estimates only and are primarily useful for identifying the major and minor constituent elements for particle-to-particle comparisons.

Elemental analyses

In addition to the microanalytical techniques discussed above, bulk analyses of carbon, hydrogen, oxygen, moisture, and ash content were determined by Coors Analytical Laboratories. This information provides insight on the organic structure and allows the determination of bulk carbon conversion.

FTIR spectroscopy

Solid-phase FTIR absorption spectroscopy was applied to Illinois #6 coal ash in collaboration with David Ottesen and Howard Johnsen of Sandia, California. By incorporating a partially reacted char sample into a KBr pressed disk and examining the transmission spectrum using an FTIR spectrometer, the existence of species with vibrational frequencies related to specific bonds can be determined. This technique can identify certain phases of interest in small concentrations; however, quantitative information is difficult to obtain and identification of all major species is not always straightforward.

X-Ray powder diffraction

In collaboration with Dale Boehme at Sandia, California, X-ray diffraction spectra were obtained for several partially reacted Illinois #6 char samples. A powder X-ray diffractometer uses essentially monochromatic X-rays to semi-quantitatively identify all crystalline phases present in significant quantities in a finely powdered bulk sample. X-ray diffraction also has the potential to reveal the degree of graphitic crystalline order in the char.

Thermogravimetric analysis (TGA)

TGA was performed on several partially-reacted Illinois #6 char samples in collaboration with Professor Jon Gibbins. This bulk technique measures the weight loss or gain of a finely ground sample as it is heated through a programmed temperature cycle. The weight change,

plotted versus temperature or residence time can then be used to derive information regarding reactivity as well as the amounts of volatile matter, fixed carbon, and ash in the sample.

Results of Sample Analyses

In this section the results of the various analytical techniques are presented and their significance for the evaluation of particle morphology and carbon/mineral matter interactions is discussed.

Particle morphology

The shape, porosity, and general appearance of the partially reacted chars can provide a great deal of useful information regarding the accessibility of the carbon in a given particle. Optical Microscopy and SEM are two valuable techniques for these purposes.

Optical microscopy. Figures 1.2 - 1.4 present optical photomicrographs of partially reacted Illinois #6 chars at various residence times. Fig. 1.2a, shows a group of representative particles from the char sample at 47 msec residence time, sampled immediately after the disappearance of the visible volatile flame. This sample comprises almost exclusively carbon-rich particles, many of which exhibit characteristic features indicating fluidity and bubble formation during devolatilization, such as large cavities and rounded protuberances. The sample at 234 msec (Fig. 1.2b) has reached a char conversion of 90% and comprises carbon-rich particles, inorganic-rich particles, mixed particle types (see Hurt and Hardesty, 1992a,b) as well as carbon fines, which are presumably fragments of the primary carbon-rich particles. The fine fragments first appear in the sample at 117 msec, and persist through 234 and 351 msec of combustion, but are absent from the sample at 468 msec.

Figure 1.3 shows a representative group of particles from a 468 msec char sample, where char carbon conversions are 96%. This sample comprises inorganic-rich and mixed particle types, with very few carbon-rich primary particles or fragments remaining. Finally, Fig. 1.4 shows a representative group of particles from the char sample in Fig. 1.3, but after removal of the residual carbon by oxidation in air at 1300 K for two hours. This procedure eliminates most of the black inclusions, which are believed to be primarily elemental carbon. A number of dark particles are still present, many having a brownish tint. Both the brown tint and initial X-ray diffraction results suggest that much of the dark material in the completely ashed sample is the high-temperature iron oxide phase maghemite, Fe_2O_3 , which is dimorphous with hematite.

Scanning electron microscopy. Figures 1.5 - 1.7 present a set of scanning electron micrographs of partially reacted Illinois #6 chars at selected residence times. Fig. 1.5 compares char particles at 47 msec (at the onset of heterogeneous oxidation) with particles at 117 msec (at the end of the first pass). The fluid history of these particles is quite evident, with solidified bubble structures prevalent on the external surfaces. At 117 msec residence time (Fig. 1.5b), the primary particles are very macroporous and may have lost a coherent

a)
 $\tau = 47 \text{ msec}$

b)
 $\tau = 234 \text{ msec}$

Figure 1.2 Optical photomicrographs of partially-reacted chars from Illinois #6 coal sampled at two residence times. Initial particle diameter 75 - 106 μm . Combustion in 12 mole-% oxygen at a nominal gas temperature 1600 K.

Figure 1.3 Optical photomicrograph of highly-reacted char from Illinois #6 coal. Initial particle diameter of 75-106 μm . Combustion in 12 mole-% oxygen at a nominal gas temperature of 1600K; 468 msec residence time.

Figure 1.4 Optical photomicrograph of fly ash from Illinois #6 coal. Initial particle diameter 75 - 106 μm . Combustion in 12 mole-% oxygen at a nominal gas temperature of 1600 K for 468 msec, followed by oxidation in air at 1300 K for two hours.

outer shell by oxidation. In addition, many carbon fragments are observed, consistent with the fragile appearance of the remaining primarily particles. It is not clear in these experiments if the fragmentation occurs during combustion or subsequently, during sample collection and handling. Indeed, recent work in this laboratory, using a new captive-particle imaging technique, suggests that very little true combustion fragmentation occurs for this char under these conditions.

Fig. 1.6 presents micrographs of the char sample at 351 msec using both secondary-electron and backscattered-electron detectors. The secondary electron detector, which yields an image brightness determined primarily by topology, highlights the complex morphology of this sample, with a broad range of particle sizes and types (Fig. 1.6a). The backscattered-electron detector, which yields an image brightness that increases with increasing sample molecular weight, reveals smooth-surfaced, inorganic-rich particles and dark, carbon-rich particles having characteristic macroporous carbon morphology (Fig. 1.6b). This

a)
 $\tau = 47$ msec

b)
 $\tau = 117$ msec

Figure 1.5 Scanning electron micrographs of partially-reacted char from Illinois #6 coal sampled at two residence times. Initial particle diameter 75 - 106 μm . Combustion in 12 mole-% oxygen at a nominal gas temperature 1600 K.

a)
secondary
electron
detection

b)
backscattered
electron
detection

c)
secondary
electron
detection;
(high mag.)

Figure 1.6 SEM images of Illinois #6 char after 351 msec combustion in 12% O₂.

characteristic carbon morphology is highlighted in the higher magnification secondary-electron micrograph in Fig. 1.6c.

Coupled optical and scanning electron microscopy. Figure 1.7 shows a single primary particle selected from the sample extracted at 351 msec residence time, mounted on a copper grid, and imaged using visible light (Fig. 1.7a) and the electron beam (Fig. 1.7b). Also shown are the results of a semi-quantitative chemical analysis of various regions of this particle, using Energy Dispersive X-ray Spectroscopy (EDS). The dark region at the top of the particle contains primarily iron, calcium, oxygen, and carbon while the bright portion of the particle contains primarily calcium, oxygen, and carbon. The brightness of the optical image in this region suggests that elemental carbon is not a major component. The approximate ratios of calcium, carbon, and oxygen in this region is consistent with a predominance of calcium carbonate. Carbonates have been detected in bulk fly ash samples from this coal by FTIR absorption spectroscopy, as discussed later in the report. Finally, several fine particles are attached to the primary particle in Fig. 1.7b that have characteristic porous carbon morphology. EDS analysis of these fine particles revealed, indeed, carbon and oxygen as the primary components.

Interaction of carbon with mineral matter

At very high conversion, the combustion reactivity of residual carbon may be greatly influenced by its interaction with mineral matter. It is possible that some fraction of the organic carbon is partially or wholly encapsulated by inorganic material, and thus quite resistant to oxidation. Indeed, significant numbers of black particles or black inclusions were observed in optical photomicrographs of all samples, including those that had been exposed to a two-hour air oxidation at 1300 K. Coupled optical microscopy and laser spark spectroscopy was therefore used to characterize the mode of occurrence of residual carbon in highly reacted Illinois #6 char samples. Of particular interest were the chemical compositions of wholly or partially black particles selected from the sample exposed to the two-hour, 1300 K oxidation in air. Selected particles were also examined from Illinois #6 char samples collected at 47 msec (immediately after devolatilization, 0% char carbon conversion) and 468 msec (late in the final burnout phase, 96% char carbon conversion).

Optical photomicrograph and corresponding atomic emission spectra are presented in Figs. 1.8 through 1.10 for several example particles from each of the samples investigated. Fig. 1.8 shows the spectrum of a char particle immediately after devolatilization ($\tau = 47$ msec), showing a relatively large amount of carbon, as expected.

Recalling the limitations mentioned previously, the NBS tables and the line intensities of these spectra can be used to estimate compositions for interparticle comparison. Although these values are accurate only for determining which particles are carbon-rich and what ash components are major/minor species, these numbers are reasonable when compared with bulk analyses and SEM microprobe work discussed previously. The char particle spectrum of Fig 1.8 yields the following compositional ratios for carbon, silicon, aluminum, and iron: 40 (C) : 4 (Si) : 4 (Al) : 1 (Fe). Other elements such as calcium, sulfur, and oxygen are present in small quantities but do not have intense lines in the wavelength region under consideration.

**Major Components
indicated by EDS :**

Figure 1.7. Images and EDS analyses of a partially-reacted char particle from Illinois #6 coal. a) optical photomicrograph, b) SEM secondary electron image. Combustion in 12 mole-% oxygen: nominal gas temperature 1600 K; residence time 351 msec.

Figure 1.8 Atomic emission spectrum from a laser-generated plasma of a typical Illinois #6 char particle collected after 47 msec combustion in 12 mole-% oxygen at a nominal gas temperature of 1600 K.

Fig. 1.9 shows three partially reacted char particles after 4 passes through the CCL flow reactor (468 msec residence time). Dark particles that potentially contain residual elemental carbon were deliberately selected. The particle shown in Fig. 1.9a appears very similar to an unreacted char particle and, indeed, the calculated composition is very similar, 40 (C) : 3 (Si) : 3 (Al) : 1 (Fe). Fig. 1.9b, conversely, shows no carbon, 0 (C) : 1 (Si) : 1 (Al) : 2 (Fe). The spherical shape of this particle implies that it existed as a liquid at some point in the combustion process, and the presence of iron-bearing phases is the likely explanation for its black color. A relatively common darker particle from this sample is shown in Fig. 1.9c. This particle appears to have dark inclusions which are at least partially carbon, 1 (C) : 2 (Si) : 5 (Al) : 1 (Fe). Although a much larger amount of carbon is present in the particle in Fig. 1.9a, mixed or inorganic-rich particles such as that in Fig. 1.9c are much more common in this sample and thus both are likely to make significant contributions to the total carbon content.

In order to better understand the mineral matter/residual carbon interaction taking place in the partially-reacted char particles after 468 msec of combustion, a portion of this sample was further oxidized in air at 1300 K for two hours. The spectra, presented in Fig. 1.10, show that significantly smaller amounts of carbon are present[†]; however, the existence of even small

[†] The height of the carbon peak located at 247.9 nm, although measurable, is not as large as it appears in Fig. 1.10 due to the presence of an iron line at 248.0 nm. The subtraction of this iron peak and the two boron peaks were a necessary part of the calculation of the carbon compositions presented herein.

Figure 1.9 Atomic emission spectra from the laser-generated plasmas of three Illinois #6 char particles collected after 468 msec combustion in 12 mole-% oxygen at a nominal gas temperature of 1600 K.

Figure 1.10 Atomic emission spectrum from laser-generated plasmas of two Illinois #6 char particles collected after 468 msec combustion in 12 mole-% oxygen at a nominal gas temperature of 1600 K and then oxidized in air at 1300 K for 2 hr.

amounts of carbon after lengthy exposure to this high-temperature oxidizing environment is surprising. This result could mean that encapsulation of the carbon is occurring, thereby preventing further oxidation of this carbon, or that the carbon is somehow being added to the sample after the ashing process. A possible ash reaction that would produce a carbon-containing species is the formation of a carbonate from calcium and carbon dioxide. Thermodynamic calculations predict that calcium would be converted to calcium carbonate in

the presence of atmospheric carbon dioxide at temperatures less than experienced during combustion and greater than room temperature. Elemental analysis indicates that calcium constitutes about 7% of the bulk Illinois #6 ash on an oxide basis. If all calcium present in the ash were converted to calcium carbonate, about 2% of the ash would be carbon. This could explain the presence of small amounts of carbon.

Figure 1.11 shows an FTIR transmission spectra for a sample that has undergone multiple capture and reinjection followed by the ashing process discussed previously. This spectrum shows that carbonate bonds are indeed present, therefore, accounting for at least some of the carbon. Thermogravimetric analysis performed on this sample supports this conclusion. Sieving was used to separate a 117 msec sample into ash-rich and organic-rich fractions and thermogravimetry in N₂ was performed on both fractions up to a maximum temperature of 1200 K. The carbon-rich portion did not experience any noticeable weight change. However, the ash-rich portion underwent a significant mass decrease with a peak loss rate at 1010 K, slightly above the 990 K temperature at which the reaction $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ is known to proceed.

Several conclusions can be drawn from this analysis of carbon/mineral interactions. Most, but not all, of the black material observed in the highly-reacted samples is elemental carbon; the remainder is comprised of primarily iron-bearing phases. The spherical, fused particles are most likely iron-containing phases bearing little or no carbon. Carbonates can form in ash samples that have been exposed to room air, which limits the accurate measurement of carbon in very highly-reacted samples. Thus for Illinois #6 coal, the accuracy of elemental carbon determination, and thus carbon conversion, is questionable for samples with less than 2% total carbon. Indeed, a fraction of the residual carbon detected in the sample at 468 msec may be carbonate carbon, and thus the quantitative accuracy of the carbon conversion at 468 msec in Fig. 1.1 is questionable. Finally, in light of these FTIR and TGA results, there is no evidence that significant amounts of elemental carbon survive the two-hour air oxidation at 1300 K. There is thus no evidence that a portion of the carbon is encapsulated and completely resistant to oxidation.

An additional conclusion can be drawn by combining the results on particle morphology and carbon/mineral interactions. In the most highly reacted sample (at 468 msec residence time) carbon is largely in the form of small or large carbon inclusions in primarily inorganic matrices. The low reactivity of these particles is easily explained by their low carbon densities, ρ_c , defined as the weight of carbon per unit volume of the particle. This carbon density is directly related to the particle combustion rate, as will be shown in the next quarterly report by an examination of the fundamental reaction/pore diffusion equations that determine the global particle reactivities. Therefore, at very high conversion the ash "dilutes" the residual carbon while maintaining a high external surface area for radiative heat loss. If for some chars, in addition, the inorganic material acts as a diffusion barrier, partially encapsulating the carbon, the particle reactivities will be lower yet.

Figure 1.11 FTIR absorption spectrum of Illinois #6 char collected after 351 msec combustion in 12 mole-% oxygen followed by air oxidation at 1300 K for 2 hr (sample mixed with KBr and pressed into a disk).

Synthesis: The Process of Char Combustion to Complete Conversion

Fig. 1.12 summarizes the process of char combustion to complete conversion, integrating all of the detailed information presented and discussed in the past several quarterly reports. A typical time scale is included in Fig. 1.12 — note that the absolute times are specific to combustion of Illinois #6 coal in 12 mole-% oxygen and a nominal gas temperature of 1600 K. After an initial period of transient particle heating and devolatilization, rapid heterogeneous oxidation begins. The rapid combustion phase lasts for a relatively short time (~ 50 msec), at which point numerous near-extinction events lead to a predominance of low-temperature particles. Many of these particles are carbon-rich as evidenced by their high emissive factors (Hurt and Hardesty, 1992a,b; Hurt, 93). Inorganic-rich particles and fragments of the primary carbon-rich particles also begin to appear at the end of the rapid combustion phase. The extent of fragmentation during the combustion process alone cannot be determined by the extractive sampling experiments, but recent results from a captive particle imaging technique suggest *limited* combustion fragmentation for this coal under these conditions. By 400 - 500 msec residence time, the primary carbon-rich particles and their fragments have

Figure 1.12 Depiction of the char combustion process to complete carbon conversion. Time scale is for combustion of Illinois #6 coal in 12 % oxygen.

largely disappeared, leaving only mixed particles types or inorganic-rich particles with residual carbon embedded in an inorganic matrix. The formation of a coherent inorganic framework in these particles stops any carbon fragmentation that may be occurring.

The burnout process described above can be conveniently divided into three stages as shown in Fig. 1.12: 1) *early char combustion*, which proceeds rapidly and at high temperature, consuming 50 - 80% of the char carbon, and ending with near-extinction of the particles as discussed previously (Hurt and Hardesty, 1992a,b, Hurt, 1993); 2) *late char combustion* which converts carbon-rich particles to mixed particles at lower temperatures and reduced rates; and 3) *decarburization of ash*, the final consumption of residual carbon imbedded in primarily inorganic matrices. This third stage is believed to be significantly slower than either of the first two stages, as recently confirmed through use of the new captive particle imaging technique mentioned previously. The char combustion process is seen to be asymptotic in nature, occurring at a continually decreasing rate as complete carbon conversion is approached. The asymptotic nature of the process is not predicted by conversion-independent global kinetic models. For the specific case of Illinois #6 coal, the global model predictions deviate dramatically from the measured rates at char carbon conversions greater than 80%. For example, the total time required for 96% char carbon conversion was measured to be a *factor of four* greater than that predicted by extrapolation of Illinois #6 global kinetics to the high conversion regime.

The underlying physical and chemical phenomena responsible for the deactivation at high carbon conversion can be classified into three groups related to: 1) particle morphology 2) carbon/mineral interactions and 3) carbon structural transformations. Further research is needed to completely characterize these phenomena, but the sample analyses performed to date do provide insight on factors 1 and 2. The initial deactivation and near-extinction cannot be explained by changes in particle macrostructure — at the relatively low conversions where the reactivity begins to change, the carbon-rich particles are highly macroporous, providing excellent access to the internal surfaces where oxidation occurs. Partial or total carbon encapsulation by inorganic material is also ruled out as the cause of the initial deactivation and near-extinction. Changes in the carbonaceous matrix are the most likely explanation for the initial deactivation and are thus the focus of current research. At very high conversion (greater than 95%), mixed and inorganic-rich particle types predominate for Illinois #6, and low particle reactivities are easily explained by low carbon densities, i.e. small amounts of residual carbon per unit particle volume in the primarily inorganic matrices. Finally, for Illinois #6 coal, there is no evidence that some portion of the residual carbon is completely resistant to oxidation due to complete inorganic encapsulation.

PLANS FOR NEXT QUARTER

Work next quarter will focus on characterizing the changes in carbon structure that occur during char combustion. The primary objective is to identify the mechanism leading to deactivation and early near-extinction. The information on carbon structure will be combined with the information presented in the current report on particle morphology and carbon/mineral interactions to develop a complete description of the char combustion process to complete

conversion. The captive particle imaging technique will be further developed and applied to several coals of varying rank.

NOMENCLATURE FOR TASK 1

q combustion rate, g-carbon/s-cm²
 T_g gas temperature, K
 T_p particle temperature, K

Greek symbols

ρ_c carbon density, g-carbon/cm³-particle
 τ residence time, msec

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ACKNOWLEDGMENTS

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PUBLICATIONS, PAPERS, AND PRESENTATIONS

This quarter, a paper on PETC-sponsored research on char combustion at high carbon conversion was presented at the ACERC Conference on Clean and Efficient Combustion of Fossil Fuels and Toxic Wastes. The paper was also presented at the Western States Section of the Combustion Institute in March and has been submitted in parallel to *Energy and Fuels*. The reference is given below.

Hurt, R.H. "Reactivity Distributions and Extinction Phenomena in Coal Char Combustion" submitted to *Energy and Fuels*, March (1993).

Also this quarter, a brief correspondence was submitted to *Combustion and Flame* on the topic of carbon structural evolution during oxidation:

Hurt, R. H., Sarofim, A. F. and Longwell, J. P. "Gasification-Induced Densification of Carbons: From Soot to Form Coke" submitted to *Combustion and Flame*, March (1993)

This note does not contain experimental results from the CCL. It is based upon earlier work by R.H. Hurt at the Massachusetts Institute of Technology and offers a reinterpretation of recent literature data and reviews the rapidly expanding literature on carbon densification.

COLLABORATIONS, VISITORS, CONTRIBUTING PERSONNEL

The collaboration with Professor Jonathan Gibbins of Imperial College, London, continued this quarter. We anticipate presenting results of his TGA experiments on partially reacted Illinois #6 coals in the next quarterly progress report. Within Sandia, California, collaborations were continued with Dr. David Ottesen (laser spark spectroscopy) Nancy Yang (SEM, TEM), Thomas Headley (HRTEM/SAED), and Dale Boehme (X-ray diffraction).

Philip Goldberg of PETC visited the Coal Combustion Laboratory and Laminar Coal Flame Reactor this quarter to discuss technical and programmatic issues and to see the new captive particle imaging experiments. Hamid Sarv of Babcock and Wilcox also visited the Coal Combustion Laboratory this quarter to discuss nitrogen release during coal combustion as well as late-stage char combustion and carbon burnout.

Task 1. Milestone Chart

Key to Milestones

- 1a. Assessment of existing kinetic models/parameters for Ill. #6 unburned carbon prediction.
- 1b. Properties and reactivity characterized for residual carbon from Ill. #6
- 1c. Properties and reactivity characterized for residual carbon from Pocahontas #3
- 1d. Assessment of existing kinetic models/parameters for Poc. #3 unburned carbon prediction.
- 1e. Auxiliary experiments complete identifying fundamental factors determining residual carbon reactivity
- 1f. Conversion-dependent reactivity correlations/models developed
- 1g. Advanced conversion-dependent, distributed-reactivity char oxidation kinetic model developed
- 1h. Model validation through predictions and measurements of MFC performance

- 2a. Particle population statistics compiled and trends identified for each of the ten coals in the PETC suite.
- 2b. Experiments completed and reactivity and property distributions computed for two of four coals
- 2c. Experiments completed and reactivity and property distributions computed for remaining two coals
- 2d. New combustion model framework developed based on single-particle kinetics
- 2e. Distributed reactivity model applied to describe the evolution of single-particle temperature distributions for two coals.
- 2f. Numerical simulations of the burnout of heterogeneous particle populations in boiler-relevant environments
- 2g. Identification of mechanisms determining unburned carbon; results of subtask input into subtask 2.1

(Continued on next page)

Task 1. Milestone Chart (Continuation)

(continued)

- 3a. Imaging system and particle suspension device installed and tested in the LCF.
- 3b. Flow reactor experiments on devolatilization/combustion transition complete
- 3c. Initial high-resolution images obtained of particle devolatilization/combustion lifetimes
- 3d. Characterization of chars and interpretation of flow reactor experiments complete.
- 3e. Comprehensive imaging study of one coal complete; parameter studies complete of the effect of oxygen concentration, gas temperature, slip velocity, and particle type
- 3f. Comprehensive imaging study of three coals complete; information input into subtask 2.1

- 4a. Unification of existing data on char reactivity complete
- 4b. Final version of Milestone report complete
- 4c. Unification of existing data on reactivity and on physical property evolution complete
- 4d. Unification of nitrogen release rates and mechanisms complete

PROJECT TITLE: COAL COMBUSTION SCIENCE

**TASK 2: THE FATE OF INORGANIC MATERIAL
DURING COAL COMBUSTION**

ORGANIZATION: Sandia National Laboratories, Livermore

CONTRACT: FWP 0709

REPORTING PERIOD: January 1, 1993 - March 31, 1993

REPORTED BY: L. L. Baxter and D. R. Hardesty

Phone: (510) 294-2862 and (510) 294-2321

OBJECTIVES FOR TASK 2

The overall objectives for FY93 are: (1) to complete experimental and theoretical investigation of ash release mechanisms; (2) to complete experimental work on char fragmentation; (3) to establish the extent of coal (as opposed to char) fragmentation as a function of coal type and particle size; (4) to develop diagnostic capabilities for *in situ*, real-time, qualitative indications of surface species composition during ash deposition, with work continuing into FY94; (5) to develop diagnostic capabilities for *in situ*, real-time qualitative detection of inorganic vapor concentrations; and (6) to conduct a literature survey on the current state of understanding of ash deposition, with work continuing into FY94.

Three subtasks are discussed below that address these objectives. The features of the work to be performed in FY93 include: (1) completion of mineral matter release studies dealing with major species; (2) studies of coal fragmentation during devolatilization; (3) collection of preliminary surface species composition data using FTIR or other real time, *in situ* optical techniques; and (4) documentation of ADLVIC.

SUBTASK 2.1 TRANSFORMATIONS: RELEASE OF INORGANIC MATERIAL DURING COAL COMBUSTION

The objective for Subtask 2.1 in FY93 is to complete experimental and theoretical investigations of the mechanisms, rates, and yields of mineral matter release from coal by inorganic and organic reactivity.

The goal of this subtask is to test the hypothesis that some inorganic species are released from coal particles during coal devolatilization and char oxidation. Particular focus is on mechanisms of release other than ash vaporization. Material release effected by coal devolatilization involves the small-grained and organically-associated minerals, many of which are strongly implicated in deposit formation in commercial-scale boilers. Mineral release associated with inorganic reactivity includes thermally unstable or chemically reactive material such as pyrite and calcite, both of which play significant roles in deposit formation and properties. This subtask uses data collected in each of the three coal reactors at Sandia and tests several ranks of coal at several rates of devolatilization.

SUBTASK 2.2 THE EVOLUTION OF PARTICLE AND FLY ASH SIZE DISTRIBUTIONS

The objectives for Subtask 2.2 in FY93 are (1) to complete the analysis of char fragmentation as a function of char structure, initial char particle size, and ash loading, and (2) to estimate the extent of coal fragmentation during devolatilization as a function of coal rank.

SUBTASK 2.3 SPECTROSCOPIC STUDIES OF INORGANIC PHASES

The objectives for Subtask 2.3 in FY93 are: (1) to demonstrate a capability to measure, qualitatively, surface species composition *in situ* and in real time in coal combustion environments (environments typical of Combustion 2000 and other technologies relevant to PETC's mission); (2) demonstrate a capability to measure, qualitatively, inorganic vapor species *in situ* and in real time in a coal combustion environment; and (3) provide documentation of past deposition work and review literature relevant to ash deposition for PETC.

SUMMARY OF TECHNICAL PROGRESS DURING THIS QUARTER

SUBTASK 2.1 TRANSFORMATIONS: RELEASE OF INORGANIC MATERIAL DURING COAL COMBUSTION

Chemical fractionation tests on coals pulverized to different sizes were completed this quarter. These data will help us to assess the accuracy of the fuels characterizations for the purpose of interpreting inorganic release during coal devolatilization. Chemical fractionation tests on mineral species are proceeding for the same purposes, but these are not yet completed. A complete report on both the chemical fractionation procedure and the release of inorganic material during coal devolatilization will be issued when the remainder of the tests are complete.

SUBTASK 2.2 THE EVOLUTION OF PARTICLE AND FLY ASH SIZE DISTRIBUTIONS

All fragmentation data have been collected. The data indicate, as in the past, that the amount of fragmentation of char particles is small compared to some previous reports. These results

are confirmed by recent captive particle imaging (see Task 1 discussion in this quarterly report) of char particles during combustion, in which no fragmentation has been observed. Fragmentation during devolatilization is still under investigation (data are all collected but analysis is not complete). These will be reported in the future.

SUBTASK 2.3 SPECTROSCOPIC STUDIES OF INORGANIC PHASES

Combustion tests of an eastern, western, and blend of coals from Northern Indiana Public Services Co. (NIPSCO) were completed this quarter. Additional western coals from Northern States Power (NSP) are under preparation for combustion tests. In both cases, the coals represent interesting and relevant fuels for Combustion 2000 equipment. In the case of the NSP coals, the fuels are reported to have very similar elemental compositions but to exhibit markedly different deposition behavior in a combustor. The FTIR analysis technique shows promise of uncovering the differences in their ash deposition behavior. These tests are designed primarily to further develop the FTIR spectroscopic technique. Issues that have been investigated this quarter include the effect of changing surface temperatures, the effect of probe emissive properties, and the effect of gas phase emission on the measured surface emission spectra.

Several analyses have also been initiated on samples of ash deposits from the three NIPSCO coals. These include diffuse reflectance FTIR analyses, atomic emission elemental analyses, x-ray diffraction analyses, and SEM/XRD analyses. These should be completed early in the next quarter and will be compared to each other and with the *in situ* FTIR results to validate the latter.

Several improvements in both experimental technique and data analysis have been completed or are in progress. These include modifying laboratory equipment in the area surrounding the deposition probe to minimize secondary reflections on the bottom of the probe, establishing blackbody reference spectra, pyrometrically measuring surface temperature, improving optical alignment, and improving our analysis of the gas-phase data. The focus of this report is on the last issue.

The following discussion indicates in some detail how the *in situ*, real-time spectra of ash deposits in the pilot-scale MFC combustor are analyzed to remove the influence of the gas phase emission. Infrared-active gas-phase species such as water and carbon dioxide are the primary contributors to the interference in the spectrometer. Detailed determination of the chemical composition of surface species requires removing or, as a minimum, distinguishing spectral features that are attributable to the gas from those of the condensed-phase deposit. The data analysis technique is first discussed using idealized spectra and then demonstrated with actual data.

One of the major challenges in analyzing data from actual combustion conditions is distinguishing gas phase emission from surface emission. The problem is illustrated in Figure 2.1, where broad, condensed-phase emission bands and narrow, gas-phase emission peaks are superimposed. These simulated data are used to illustrate several aspects of

spectral analysis because they can easily be separated into simulated gas- and condensed-phase components. They resemble actual data, as will be illustrated later. The condensed-phase emission consists of three Gaussian profiles and two Lorentzian profiles. The Gaussian profiles are centered at 500, 570, and 600 cm^{-1} with widths (one standard deviation) of 40, 200 and 5, cm^{-1} , respectively. The Lorentzian profiles are centered at 700 and 800 cm^{-1} with widths (full width at half height) of 25 and 15 cm^{-1} , respectively.

Also shown in the figure are several gas-phase emission lines. These appear as sharp peaks. In fact, they have line widths (FWHM) equal to about one half of the resolution of the spectrum. Emission bands from actual gas-phase species are significantly narrower than the resolution at which the spectra are collected ($\approx 1 \text{ cm}^{-1}$ in this case). The positive-going gas-phase emission lines are located at 450, 487, 492, 545, 605, 650, 702, 750, 795, 805, and 810 cm^{-1} . There are also two negative-going peaks located at 510 and 705 cm^{-1} . Gas temperatures exceed surface temperatures by several hundred degrees in these experiments ($T_g \approx 900 \text{ }^\circ\text{C}$, $T_s \approx 450 \text{ }^\circ\text{C}$). Therefore, gas phase emission is more intense than surface emission, producing positive-going peaks. However, many of the emitting gases are also present in the relatively cool atmosphere between the reacting flow and the interferometer. These cool gases tend to absorb emitted radiation, producing negative-going peaks. In the spectral regions of greatest interest to us, there tend to be more positive-going peaks arising from hot-band and high-energy upper state transitions (which have less significant absorption at room temperature) than negative-going, self-absorbed lines.

The distinguishing characteristic between condensed- and gas-phase emission is the width of the features. Individual gas-phase emission lines have widths on the order of 0.05 cm^{-1} under these combustion conditions ($T_g \approx 900 \text{ }^\circ\text{C}$; $P_g = 1 \text{ atm.}$). By contrast, condensed-phase bands have typical widths of at least 10 cm^{-1} and more commonly 50-100 cm^{-1} or greater under similar conditions. These characteristic spectral widths relate to the variation in energy levels associated with the quantum transitions of the molecules. Since condensed phase materials are influenced by far more neighboring atoms and suffer collisions at much higher rates than gas phase materials, their lines are typically very broad. Time between gas-phase collisions greatly exceeds that of molecules in the condensed phase, and transitions in gas phase species are only modestly influenced by neighboring gas molecules, principally because of their substantially lower molecular density. Hence, gas-phase species have more well defined energy levels and narrower line widths [Berry, et al., 1980; Bohren and Huffman, 1983].

One approach to removing the gas phase interference is to measure it separately from the condensed phase emission by placing a nonemitting (cold) surface immediately in front of the emission probe. This is easily accomplished in the MFC because of the convenient optical and physical access. It is less practical in other pilot-scale or full-scale devices. However, the turbulent fluctuations of the gas species introduce enough variation in the measurements that one cannot reliably eliminate the emission in this way. Furthermore, this approach to eliminating the emission, even if the gas-phase spectrum could be perfectly reproduced at each measurement time, only results in changing largely positive-going peaks in the spectrum into negative-going peaks of equal or greater relative magnitude.

Figure 2.1 Typical but artificially produced single beam spectrum of condensed phase ash deposits superimposed with gas-phase emission spectra under conditions typical of the pilot-scale MFC combustor. Condensed-phase bands consist of two Lorentzian profiles and three Gaussian profiles. The narrow peaks are gas-phase emission.

What is needed is a means of removing the peaks in the sense of replacing them by interpolated data, with the interpolation being performed between the baseline points around the base of the peak. This type of data analysis we will call clipping. It is contrasted to smoothing, where the peak area is spread out over the surrounding area. Both data analyses are conveniently done with Fourier transforms [Bracewell, 1978], and such transforms are used in the approach we are taking. (Clipping of a spectrum is a potentially confusing term. The term clipping is sometimes used to refer to intentionally or unintentionally reducing the maximum intensity of spectral lines by, for example, saturating a detector. This is an entirely different issue than removing the lines from the spectrum.)

We first illustrate the potential problems associated with smoothing data and then illustrate an algorithm we recently developed that largely eliminates the problem.

Problems Associated with Smoothing Spectral Data in This Experiment

Conservation of total area under a peak.

The intensity of gas emission is sufficient to completely obscure any surface information in the untreated spectrum. However, the surface emission is always broader than any individual gas emission peak. Therefore, if the gas emission lines are sufficiently separated, we can reasonably estimate the surface emission in the region of a gas emission peak by removing the peak and interpolating between surface emission signals on either side of it.

Removing the gas emission lines, which are characterized by large and sharp departures from an otherwise smoothly varying baseline, can be accomplished by several means. The most common is to use a data smoothing algorithm [Burden, et al., 1981; Griffiths and de Haseth, 1986; Press, et al., 1992]. The result of smoothing the data in Fig. 3.1 using one of the more sophisticated smoothing algorithms (convolution with a binomial distribution) is illustrated in Fig. 2.2 for typical and extreme smoothing. The original data are shown as dashed lines, with a moderately smoothed result (5 passes) indicated by a dotted line and the strongly smoothed result (70 passes) being indicated by a solid line.

Figure 2.2 Data from Fig. 2.1 (dashed line) after moderate smoothing (dotted line) and strong smoothing (solid line).

It is clear that the smoothing algorithm has substantially reduced the magnitude of the gas-phase peaks. A more detailed examination, for example in the region around 600 cm^{-1} , illustrates some of the details of the smoothing algorithm (Fig. 2.3). Two observations relative to the analysis of our data are significant. At moderate smoothing, the broad features are relatively unchanged whereas at strong smoothing, even the broad bands are noticeably altered. More importantly, both smoothing algorithms have the effect of smoothing the peaks over a wider wavenumber region rather than removing them. This is a common feature of most smoothing algorithms. That is, the area under a curve doesn't change with smoothing, but the variation in the slope of the curve diminishes.

Figure 2.3 Details of data from Fig. 2.2 between 615 and 595 cm^{-1} .

Introduction of Artificial Features in Final Data

As time progresses, the condensed phase emission changes due to chemical reactions or physical transformations of the deposit or deposition of new material on the surface. However, the MFC is operated at steady state. Therefore, changes in the magnitude of gas emission are much smaller and arise only because of turbulent fluctuations in gas composition and temperature. There should be no discernable changes in the spectral location of the gas-phase peaks.

We determine surface composition by ratioing an experimental spectrum from an unknown sample with that from some reference sample (a blackbody or the clean probe surface) and multiplying the result by the reference emissivity. The resulting spectrum is the emissivity of the deposit as a function of wavenumber. Since the unknown (deposit) signal has different spectral characteristic than the reference, the composition of the unknown material can be determined by assigning peaks of the resulting spectrum to chemical species known to emit radiation at the same locations.

Figure 2.4 Two examples of experimental spectrum ratioed to reference spectrum. In one case, both were smoothed using a typical algorithm (solid line). The second case illustrates the actual ratio when gas-phase interference is ignored (dashed line).

The results of ratioing two smoothed spectra similar to that shown in Fig. 2.3 (smoothing with 70 passes in each case) are illustrated in Figs. 2.4 and 2.5. The spectra differ in that they simulate different times in the progression of growing an ash deposit. The intensities of the four narrowest condensed-phase bands increase by a factor of 1.1, whereas the intensities of the gas phase peaks and the broadest condensed-phase band remain constant, since the gas-phase environment does not change with time.

In general, the gas-phase interference only modestly compromises the condensed-phase spectra. However, even these modest compromises can make interpretation of the condensed-phase spectra difficult. To illustrate, a careful examination of the ratio spectrum in the region of 700 cm^{-1} is compared with the actual changes (Fig. 2.5). Figure 2.5 indicates that the band near 700 cm^{-1} could easily be mistaken for the sum of three broad bands located at 685 , 695 , and 710 cm^{-1} . These changes in apparent location of the peak maximum are large enough to cause possible erroneous assignments of species. The origin of the apparent structure in the spectrum illustrated in Fig. 2.5 is the gas phase emission/absorption. The structure could be eliminated if an analysis algorithm could be found or developed that removes the peaks from the spectrum rather than smoothing them over a broad range of wavelengths. This was the goal of our data analysis development this quarter.

Figure 2.5 Details of data shown in Fig. 2.4 in the region of 700 cm^{-1} .

Data Clipping Algorithm

Over the last quarter we have made steady progress toward developing such an algorithm. (We could find none in either original-domain filtering literature or Fourier-filtering literature that did not ultimately smooth the data rather than clip the high frequency points). Improvements have been made in stages. Here we will present the algorithm as it currently stands.

The first stage of the algorithm is to convolve the spectrum with some suitable function that removes the high frequency component of the data. This is most easily done by multiplying the Fourier transform of the original data by some filtering function that is real (the Fourier transform has both real and imaginary components), and even about the origin ($f=0$) in the frequency domain. A square wave is the ideal filtering function in the sense that it removes all frequencies above some critical value and none below it. However, it also introduces a low frequency ringing in the baseline of the resulting spectrum. This ringing is attributed to the discontinuous first derivative of the square wave function. Alternative functions we have investigated include triangular, Gaussian, and sinc [$\sin(x)/x$] functions. The latter two are by far superior in the sense of filtering high frequency components without introducing ringing. The data shown below use the Gaussian filtering function.

The filtered spectrum results in a smooth version of the original spectrum. However, all of the filtering functions have a value of unity at zero frequency in Fourier space. Therefore, the total area under the smoothed spectral signature is identical to that under the original spectrum. That is, thus far we have smoothed, and not clipped, the high frequency peaks in the spectrum, producing a result only marginally superior to that shown in Fig. 2.3.

The second step of the algorithm is to compute a unipolar difference between the original data and the smoothed data according to the formula

$$d_1 = \max[0, (s_o - s_{sm})] \quad (2.1)$$

where s represents spectrum, and subscripts o and sm represent original and smoothed, respectively. The function d thus computed will be a series of positive peaks located precisely where the narrow peaks in the original data are located with no broad-band contribution to either side of the narrow peaks. If subtracted from the original data, it will produce a spectrum that is unaltered anywhere except under the narrow peaks. Repeated smoothing of this sort will lead to total elimination of the narrow peaks with no distortion of the surrounding broad peaks, which is the filtering function we seek. However, it will only work perfectly if the narrow peaks are positive going. If the narrow peaks are all negative going, a similar filter could be derived that is similarly effective by reversing the order of subtraction within the $\max$ operator. That is

$$d_2 = \max[0, (s_{sm} - s_o)] \quad (2.2)$$

In some spectral regions, gas-phase peaks are both positive and negative going, depending on the extent of absorption by room-temperature gases. Our current algorithm first corrects

the positive going peaks, and then the negative. This subtracts the positive peaks from the data perfectly (in principal), but leaves a small, broad-band distortion of the original data around the negative peaks.

Figure 2.6 illustrates the result of applying this clipping algorithm to the data of Fig. 2.1. The positive-going peaks have been clipped, being replaced by points interpolated between the data on either side. This is nearly ideal performance with respect to the positive-going peaks. The negative going peaks are less ideal. While their magnitude has also decreased, there is significant smoothing of these peaks rather than clipping (Fig. 2.7). A second algorithm has also been developed based on the convolution of a binomial distribution with coefficients from Pascal's triangle with the data. The results from this algorithm are presented in Figs. 2.8 to 2.10. In all figures, the dotted line indicates the results from smoothing alone for comparison.

The clipping algorithms effectively remove positive-going peaks rather than smoothing them into surrounding wavenumbers. Negative-going peaks are partially removed and partially smoothed. The net effect on the overall analysis of data is illustrated in Fig. 2.11, which should be contrasted with Fig. 2.5 for a comparison of smoothing and clipping data. The clipping algorithm has improved the result, as anticipated. However, the smoothing associated with the negative values still gives rise to distortions.

An overall view of the results from the clipping algorithms is illustrated in Fig. 2.12. There are only slight differences in the performance of the binomial- and Gaussian-based algorithms. (The illustrated data were clipped using the binomial algorithm.)

Figure 2.6 Comparison of smoothing and clipping algorithms on data of Fig. 2.1

Figure 2.7 Detailed view of positive and negative-going peaks around 700 cm⁻¹.

Figure 2.8 Clipping of data in Fig. 2.1 using a binomial distribution.

Figure 2.9 Detailed view of data from Fig. 2.8 around 800 cm⁻¹ (comp. Fig. 2.10).

Figure 2.10 Spectrum near 700 cm⁻¹ illustrating distortion around negative-going peaks.

Figure 2.11 Details in the region of 700 cm⁻¹ of changes in signal.

Figure 2.12 Overall performance of clipping algorithms compared to actual changes.

Analysis of Real Data

The performance of the algorithms on real data is illustrated in Fig. 2.13. The data represent a single beam spectrum collected at 0.5 cm^{-1} with no apodization from an ash deposit generated in the MFC by a powder river basin coal (Wyodak). This is one of the two spectra that are ratioed in calculating the spectral emissivity and determining surface composition. Combustion gas temperature is about 850°C , particle burnout of fly ash approximately 99 %, and probe surface temperature approximately 450°C .

Three spectra are shown. The top spectrum is the raw data with its typical complement of gas-phase emission peaks. Essentially all of the gas emission peaks in this region are positive-going. The second line is the clipped version of the raw data, offset by -0.1 V so that it can more clearly be seen. The third line represents smoothed data, offset by -0.2 V . The smoothed data are substantially influenced by the gas emission lines in a large number of regions. The clipping algorithm has almost entirely removed this influence.

Figure 2.13 An example of raw, clipped, and smoothed data from an ash deposit in the MFC.

Residual peaks remain in the clipped version at approximately 1010, 850, 780 and 770 cm^{-1} . The baseline of the raw data also rises in these regions. Therefore, the clipping algorithm is performing correctly. However, not every rise in the baseline is associated with condensed-phase emission. Some are associated with unresolved gas-phase emission lines. The algorithm cannot distinguish between these two types of departures from the relatively smooth and broad curvature in this region.

Typically, the data we collect contains only positive-going peaks in all regions between 450 and 1300 cm^{-1} except in the vicinity of 670 cm^{-1} . An important remaining question is whether the gas emission lines can be sufficiently isolated to clearly distinguish a condensed-phase emission background. Since the gas emission lines are generally much narrower than the maximum resolution of the instrument, increasing the resolution at which the data are collected will increase their magnitude and decrease their width. Figure 2.14 illustrates two spectra of an ash deposit separated in time by a small amount but otherwise obtained under the same conditions of gas temperature, composition, and velocity. The dotted line is data collected with a resolution of 2 cm^{-1} (data point every 1 cm^{-1}) and the solid line at 0.5 cm^{-1} . Published reference spectra for condensed-phase species are typically reported with resolutions of either 8 or 4 cm^{-1} .

Figure 2.14 Comparison of 0.5 and 2 cm^{-1} resolution data over a small region of the infrared spectrum.

The interferometer being used in this study is capable of 0.1 cm^{-1} resolution, although 0.25 cm^{-1} is easier to deal with. There is little motivation to collect spectra at a resolution greater than that required to clearly identify a baseline behind the gas emission peaks. Reasons not to collect higher resolution data include (1) longer times required to collect the data, (2) longer files to store and manipulate, (3) decreased signal to noise ratio for the same total collection time, and (4) decreased ability to resolve the temporal changes on the surface because of the first two issues.

None of the spectra illustrated here have been apodized. Apodization is a mathematical manipulation of FTIR data that causes the lines to resemble those collected from a grating spectrometer and decreases the structure in the baseline around the peak. Apodization also increases the peak width. A fraction of the apparent noise in the baseline immediately surrounding an emission peak is due to the $\text{sinc}(x)$ line shape of the unapodized spectrum. The noise in the baseline, whether apparent or real, is removed during the clipping process described above.

The increased resolution from 2 to 0.5 cm^{-1} of the spectrum improves our ability to clearly distinguish the baseline from the peaks. By decreasing the number of replicate scans from 256 to about 64, we can collect the spectrum in the same amount of time and still achieve high signal to noise ratios.

The peaks in the low resolution spectrum correspond as precisely as the resolution allows with those in the higher resolution spectrum, reflecting the consistency of the gas-phase emission. At higher resolution, the magnitude of the peaks is larger and their width is narrower, as anticipated. Also, the baseline around the peaks, which results from condensed-phase emission, is more well defined in the higher resolution data.

The combination of resolution, probe configuration, and data analysis currently in use allows us to reliably interpret data collected from 450 cm^{-1} to about 1300 cm^{-1} , with the exception of the region around about 670 cm^{-1} where there is insufficient baseline between emission peaks. We can also examine the region from about 1700 cm^{-1} to about 3800 cm^{-1} , although there is little of interest in this region. The current capabilities allow detection of silicates, sulfates, some oxides (silica), carbonates, and other species of interest. However, there are several peaks of interest in the 670 cm^{-1} and beyond 1300 cm^{-1} . These regions are especially useful in detailed determination of compositions. Gas phase emission in the remaining regions is so intense that we hold little hope of collecting condensed phase information in the current configuration. Therefore, we intend to construct a probe that will dramatically reduce the path length of emitting gas, and hence the intensity of its emission, in an effort to access these regions. Details of the probe design will be presented in the future.

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PLANS FOR NEXT QUARTER

Work in the next quarter will focus on analysis of fragmentation and inorganic release of material from coal for the entire suite of coals studied in the MFC. Also, final versions of future program plans will be prepared next quarter.

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Many of the chemical and physical analyses of solid samples of fly ash, deposits, and raw coal gathered during this work are performed by CONSOL Inc. Galen Richards (Graduate Student, BYU) is taking a leading role in performing the FTIR measurements in the combustor. Gian Sclipa (Contract Technician) and Al Salmi (Technician) were also instrumental in operating and maintaining the combustor this quarter and in design and construction of diagnostic and probe equipment.

PRESENTATIONS AND PAPERS

The following presentations and papers based in whole or in part on PETC-supported work were made in the last quarter.

Baxter, L. L., "Behavior of Inorganic Material During Solid Fuel Combustion," ACERC/BYU Seminar, Brigham Young University, Feb. 11, 1993.

Baxter, L. L., and W. A. Fiveland, "Predicting the Effects of Ash Deposition on Boiler Performance," Presented at The Sixth Utility Coal Conference, St. Louis, Missouri, February 22-25, 1993.

Baxter, L. L., "Anticipation of Ash Deposition Behavior in Coal-Fired Boilers Based on Properties of Coals and Coal Blends," The Economic and Environmental Aspects of Coal Utilization V, Engineering Foundation Conference, Santa Barbara, CA, Jan. 31-Feb. 5, 1993.

Richards, G. H., D. K. Ottesen, J. N. Harb, and L. L. Baxter, "*In situ*, Real-Time Characterization of Coal Ash Deposits in a Pilot-Scale Combustor Using Fourier Transform Infrared Emission Spectroscopy," presented at the 7th Annual ACERC Conference on clean and Efficient Combustion of Fossil Fuels and Toxic Wastes, March 2-5, 1993 and to be submitted to *Energy and Fuels*.

Baxter, L.L., "Ash Deposition During Biomass and Coal Combustion: A Mechanistic Approach," *Biomass and Bioenergy*, 4:85-102 (1993).

Baxter, L.L., and R. W. DeSollar, "A Mechanistic Description of Ash Deposition During Pulverized Coal Combustion: Predictions Compared to Observations," accepted for *Fuel*, (1993).

Baxter, L.L., T. H. Fletcher, and R. E. Mitchell, "Release of Inorganic Material During Coal Devolatilization," accepted for *Combustion and Flame*, (1993).

Baxter, L.L., and R. W. DeSollar, "Ash Deposition from a Western Coal Fired in an Eastern Boiler — Predictions Compared to Measurements," submitted to *Prog. in Energy and Comb. Science*, 1993.

INITIAL DISTRIBUTION

Ms. Kay Downey (2)
MS 58-M217
U.S. DOE/PETC
P.O. Box 10940
Pittsburgh, PA 15236-0940

Mr. James M. Ekmann
Director, Coal Combustion Division
U.S. DOE/PETC
P.O. Box 10940, MS 84-307
Pittsburgh, PA 15241

Mr. Charles Garrett
Office of Technical Coordination
U.S. DOE/GTN
Fe 14, Room B-107
Washington, DC 20545

Mr. Philip M. Goldberg (2)
Coal Utilization Division
U.S. DOE/PETC, 922-H
P.O. Box 10940
Pittsburgh, PA 15236-0940

Mr. James Hickerson
Coal Utilization Division
U.S. DOE/PETC, 922-H
P.O. Box 10940
Pittsburgh, PA 15236-0940

Mr. James Jovanovich
PM-01, MS922-206
U.S. DOE/PETC, 922-H
P.O. Box 10940
Pittsburgh, PA 15236-0940

Professor Robert Essenhigh
Mechanical Engineering Department
Ohio State University
206 West 18th Avenue
Columbus, OH 43210

Professor Thomas H. Fletcher
Chemical Engineering Department
Brigham Young University
350 CB
Provo, UT 84602

Dr. Michael L. Jones
Energy and Mineral Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, ND 58202
Attn: Dr. Steve Benson

Professor John P. Longwell
Chemical Engineering Department
Massachusetts Institute of Technology
Room 66554
Cambridge, MA 02139

Professor Reginald E. Mitchell
High Temperature Gasdynamics Lab
Stanford University
Mechanical Engineering Department
Palo Alto, CA 94305

Professor Ronald Pugmire
Vice President for Research
University of Utah
210 Park Building
Salt Lake City, UT 84112

Professor Daniel E. Rosner
Director, High Temperature Chem Engr Lab
Yale University
P.O. Box 2159
New Haven, CT 06520-8167

Professor Adel Sarofim
Department of Chemical Engineering
Massachusetts Institute of Technology
66-466
Cambridge, MA 02139

Professor Philip Smith
Department of Chemical Engineering
University of Utah
2250 Merrill Engineering Bldg
Salt Lake City, UT 84112

Professor L. Douglas Smoot, Dean
College of Engineering & Technology
Brigham Young University
270 CB
Provo, UT 84602

Mr. Charles L. Wagoner, Mgr
Fuels & Combustion Sec.
University of Tennessee Space Inst
BH Goethert Parkway
Tullahoma, TN 37388

Professor Terry Wall
Department of Chemical & Materials Engr.
The University of Newcastle
Newcastle, NSW 2308
Australia

Professor Jost Wendt
Department of Chemical Engineering
University of Arizona
Tuscon, AZ 85721

Dr. Seymour B. Alpert
P.O. Box 10412
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94308

Dr. Bernie Zak
Sandia National Laboratories
Org. 6612
P.O. Box 6612
Albuquerque, NM 87185

Dr. Arthur Boni, President
PSI Technology Company
20 New England Business Center
Andover, MA 08180
Attn: Dr. Joseph Helble
Dr. Connie Senior
Dr. Srivats Srinivasachar

Mr. Richard W. Borio
Combustion Engineering Inc.
1000 Prospect Hill Road, P.O. Box 500
Windsor, CT 06095
Attn: Mr. Michael Hargrove

Mr. Richard Bryers
Foster Wheeler Development Corp.
Applied Thermo & Processes Dept.
12 Peach Tree Hill Road
Livingston, NJ 07039

Mr. Richard W. DeSollar
Fuels Coordinator
Central Illinois Public Service Co.
607 East Adams Street
Springfield, IL 62701

Mr. Larry Dorra
Engineering Supervisor
Northern Indiana Public Service Co.
P.O. Box M-720
Gary, IN 46401

Mr. Peter Torslev Jensen
ELSAM
Fuel Department
DK-7000 Fredericia
Denmark

Dr. Flynt Kennedy, Vice President
Research & Development
Consolidation Coal Co.
4000 Brownsville Road
Library, PA 15129
Attn: Dr. Anthony Fonseca

Dr. John S. Maulbetsch
Exploratory Research
EPRI
3412 Hillview Avenue
Palo Alto, CA 94303

Dr. Arun K. Mehta
P.O. Box 10412
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94308

Dr. Thomas Milne
National Renewable Energy Lab
1617 Cole Boulevard
Golden, CO 80401

Mr. Eric H. Reichl
P.O. Box 472
Princeton, NJ 08542

Dr. Dan Seery
United Technologies Research Center
Combustion Sciences
Silver Lane, MS 30
East Hartford, CT 06108

Mr. Ian W. Smith, Manager
Coal Utilization Program
CSIRO
51 Delhi Road, P.O. Box 136
North Ryde, NSW, 2113
Australia

Mr. Stanley Vecchi, Director
Energy Systems Lab/Research Dev Div
Babcock & Wilcox
1562 Beeson Street
Alliance, OH 44602

Attn: Mr. Thomas Morris Mr. James Warchol
Mr. Larry Rodgers Mr. Ralph Bailey
Dr. Hamid Sarv Mr. George Farthing

Dr. Harold W. Wahle, Manager
Heat Transfer & Fluid Mech.
Babcock & Wilcox
1562 Beeson St.
Alliance, OH 44601
Attn: Dr. Woodrow Fiveland
Mr. John Berthold

MS0735 D.E. Arvizu, 6200
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