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Coal Combustion Science Quarterly Progress Report April-June 1993

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

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT

APRIL — JUNE 1993

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Research supported by the United States Department of Energy,
Office of Fossil Energy, Pittsburgh Energy Technology Center

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT — APRIL - JUNE 1993

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This document is a quarterly status report of the Coal Combustion Science Project that is being conducted at the Combustion Research Facility, Sandia National Laboratories, Livermore, California. The information reported is for the period April - June 1993.

The objective of this work is to support the Office of Fossil Energy in executing research on coal combustion science. This project consists of basic research on coal combustion that supports both the Pittsburgh Energy Technology Center (PETC) Direct Utilization Advanced Research and Technology Development Program, and the International Energy Agency (IEA) Coal Combustion Science Project. Specific tasks include:

Task 1: Kinetics and Mechanisms of Pulverized Coal Char Combustion

The objective of this task is to characterize the combustion behavior of selected U.S. coals under conditions relevant to industrial pulverized coal-fired furnaces. Work is being done in four areas: (a) kinetics of heterogeneous fuel particle populations; (b) char combustion kinetics at high carbon conversion; (c) the role of particle structure and the char formation process in combustion and; (d) unification of the Sandia char combustion data base. This data base on the high temperature reactivities of chars from strategic U.S. coals will permit identification of important fuel-specific trends and development of predictive capabilities for advanced coal combustion systems. The principal investigator on this task is Robert H. Hurt.

Task 2: Fate of Inorganic Material During Coal Combustion

The objective of this task is to establish a quantitative understanding of the mechanisms and rates of transformation, fragmentation, and deposition of inorganic material during coal combustion as a function of coal type, particle size and temperature, the initial forms and distribution of inorganic species in the unreacted coal, and the local gas temperature and composition. In addition, optical diagnostic capabilities are being developed for *in situ*, real-time detection of inorganic vapor species and surface species during ash deposition. The principal investigator on this task is Larry L. Baxter.

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT APRIL — JUNE 1993

EXECUTIVE SUMMARY

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

Work in the Coal Combustion Laboratory this quarter focused on Subtasks 1.2 and 1.3. Under the latter subtask the role of particle structure in the char formation process is being examined. This quarter the captive particle imaging experiment was upgraded to allow simultaneous dual video imaging using particle incandescence in the near infrared along one optical path and reflected visible light along a second path. A long focal length microscope was coupled to a photoquadrocular head, modified to incorporate 40 mm diameter optical filters. The modified quadrocular head houses a beam splitter that projects identical images to two photography ports. One port is equipped with a Schott red glass filter that passes wavelengths greater than 700 nm and a monochrome frame-transfer CCD camera connected to a digital image acquisition system. The video images from this port are the result of particle incandescence from 700 nm to about 1000 nm, the long-wavelength cutoff of CCD chip sensitivity. The brightness of these images is related to particle temperature and thus to combustion rate, and the images will provide useful information on single-particle combustion and extinction behavior. It is planned to calibrate the system with a high-temperature black-body source, modified to accommodate microscope optics. The calibration may allow quantitative interpretation of the brightness levels.

A color CCD camera is attached to the second port to image visible light, supplied by a fiber-optic illuminator and reflected from char particle surfaces. These images are useful for tracking detailed changes in particle morphology during char oxidation, including the transition from carbon-rich to inorganic-rich particles with the concomitant changes in reflectance properties. A complete description of the experiment will be presented with the first set of results in the next quarterly report.

Under Subtask 1.2 we are determining char combustion kinetics to high carbon conversion. Work this quarter continued on characterizing the properties of the carbonaceous matrix of coal chars as a function of extent of combustion. This work is part of an effort, initiated last quarter, to explain the loss of reactivity and early extinction observed at high conversion for a variety of coal chars described in previous reports. Numerous sets of partially-reacted chars were examined over the course of this study, including six sets from PETC-suite coals (Illinois #6, Pittsburgh #8, Lower Kittanning, Pocahontas #3, Dietz, and Beulah lignite) and two sets from Lower Freeport and Eagle seam bituminous coals. A sequence of partially-reacted chars from Illinois #6, PSOC-1493 were characterized in the most detail.

On the basis of our work during this (and the past) quarter we identify three primary factors that combine to make coal chars progressively less reactive as the process of high temperature combustion proceeds. The three factors are:

1. Evolution of the organic molecular structure. The composition and crystalline structure of the carbonaceous organic matrix evolves during the char oxidation phase. Atomic-scale rearrangements are observed to occur in the first 70 msec of the char combustion phase (here between 47 and 117 msec total residence time with particle temperatures from 1600 - 1900 K) leading to a gradual loss of hydrogen, coalescence of aromatic structures, and turbostratic crystallite growth. This pregraphitization brings about loss of microporous surface area and a likely reduction in the intrinsic reactivity of the surfaces.
2. Loss of carbon availability. Carbon availability, expressed as m_c / V_p , with units of grams of carbon per unit particle volume, decreases as carbon atoms are consumed by oxidation. This effect is only modest at low-to-intermediate conversions or for low ash content materials, but can become quite significant for high ash content materials at high conversion (>90%). At very high conversion, residual carbon can occur primarily as inclusions in coherent inorganic frameworks. Such particles have very low carbon availabilities and thus very low global reactivities.
3. Low reactivity particles or subparticle regions present in the young char, at least some of which are derived from inertinite-rich coal particles, become enriched in the highly reacted residue due to their longer burnout times. Inertinite enrichment contributes to low reactivities at high conversion, but cannot, alone, explain the near-extinction phenomena, as the degree of enrichment and the reactivity differences between inertinite and vitrinite-derived chars are typically not large enough.

The loss of reactivity by factor (1) is primarily governed by the temperature history of the char particles, while factors (2) and (3) are primarily governed by the extent of oxidation. Further work is necessary to quantify the relative importance of these three factors, and to formulate time and conversion-dependent kinetic models to account for them.

Task 2: The Fate of Mineral Matter

During this quarter, preparation was begun of the final reports describing our work under the first two subtasks: (1) Transformations: Release of Inorganic Material During Coal Combustion and (2) The Evolution of Particle and Fly Ash Size Distributions. These reports will be completed and delivered to PETC for review during the next quarter.

In addition, progress continued on the third subtask, in which we are developing spectroscopic techniques to determine the composition of inorganic phases within ash deposits. During the quarter improvements were completed to the FTIR-based diagnostic. The operation of the modified FTIR system is described in this report. Analysis of previously acquired data, as well as new data obtained during this quarter with the improved system, is described in some detail. We also describe here the design of the new ash deposit probes that were used this quarter. The new probes permit data to be obtained in the Multifuel Combustor at higher probe surface temperatures

and also allow greater flexibility in controlling these surface temperatures. Our new blackbody radiation source was used this quarter to calculate instrument response functions and background radiation contributions over a range of temperatures. These calibration data facilitated development of a quantitative means of measuring deposit emissivities. Using the upgraded experimental features and blackbody reference technique, work continued this quarter to identify specific chemical species in FTIR spectra collected *in situ* from ash deposits created during the combustion of one coal and one coal blend. The Wyodak coal used is a sub bituminous, western U.S. coal from the Powder River Basin (PRB); the coal blend is a mixture of Eagle Butte (also a PRB coal) and Kentucky #9. The latter is a high-volatile bituminous US coal. The data obtained demonstrate that the *in situ* FTIR diagnostic can successfully detect the presence of major classes of compounds (oxides, silicates, sulfates) as well as specific species within these classes (e.g. silica, kaolinite, anhydrite, and glauberite). In addition, the time dependence of the formation of ash species on probe surfaces can be resolved. The utility of the method for bulk deposit analysis is less certain, since it is primarily sensitive to surface (100 μm to 1 mm) rather than bulk composition. The dependence of the results on composition becomes more complex for thick deposits.

Finally, during this quarter a revised project plan detailing work proposed to be performed over the next four years under this task was submitted to PETC for review and approval.

Future Work

On the char combustion task, during the next quarter the insights that we have obtained on the mechanisms of reactivity loss will be used to design auxiliary experiments and/or analyses to quantitatively characterize each of the three critical factors. These experiments will provide the data necessary for formulating an advanced, conversion-dependent kinetic model. Also next quarter, the new captive particle imaging technique will be applied to chars from Illinois #6 coal and one low rank coal to be chosen. This work should provide critical information on extinction mechanisms and the effects of coal heterogeneity. Finally, a heated chimney is being constructed to greatly extend the residence times available in a single pass in the CCL. Extractive sampling will be performed with the heated chimney to determine weight loss profiles for Illinois #6 for comparison to those determined by multiple capture and reinjection.

On the mineral matter task, work in the next quarter will focus on completing two major reports: the final report dealing with release mechanisms of inorganic materials from during coal combustion and the final report on coal and char fragmentation. These reports will summarize the results obtained in the MFC and will be accompanied by mechanistic interpretations of trends in the data. Also in the next quarter, a summary of progress under this project to date will be presented at the Ninth Annual Coal Preparation, Utilization, and Environmental Control Contractors Conference, in Pittsburgh, PA, July 19-22, 1993. The paper and presentation materials to be used during this conference have been forwarded to PETC for review. Finally, experiments dealing with two Powder River Basin coals, Black Thunder and Antelope, will be conducted to determine the FTIR diagnostic technique is capable of detecting differences in their behavior. These coals are reported to be nearly identical in their elemental analysis yet commercial experience indicates that their ash behavior is quite different.

PROJECT TITLE: COAL COMBUSTION SCIENCE

**TASK 1: KINETICS AND MECHANISMS OF
PULVERIZED COAL CHAR COMBUSTION**

ORGANIZATION: Sandia National Laboratories, Livermore

CONTRACT: FWP 0709

REPORTING PERIOD: April 1 - June 30, 1993

REPORTED BY: R. H. Hurt, K. A. Davis, and D. R. Hardesty

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OBJECTIVE FOR TASK 1

The objective of Task 1 is to characterize the combustion behavior of selected U.S. coals under conditions relevant to industrial 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 combustion environment. Partially reacted char particles are also sampled and characterized with advanced materials diagnostics to understand the critical physical and chemical transformations that influence reaction rates and burnout times. The ultimate goal of the task is the establishment of a data base of the high temperature reactivities of chars from strategic U.S. coals, from which important trends may be identified and predictive capabilities developed.

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 pulverized coal combustion the process of devolatilization determines, to a large extent, the properties and thus the reactivity of the resulting char. Swelling coals, in particular, produce a variety of char particle morphologies ranging from dense consolidated particles to thin or thick walled cenospheres, depending in part on devolatilization conditions. The objective of this subtask is to generalize the kinetic results obtained in the CCL to other devolatilization and combustion environments, through an improved understanding of the char formation process and its relationship to char combustion rates and burnout times. This will be achieved through a combination of flow reactor experiments and high-resolution single-particle imaging.

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 in the Coal Combustion Laboratory this quarter focused on subtasks 1.2 and 1.3, as described below.

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

The captive particle imaging experiment was upgraded this quarter to allow simultaneous dual video imaging using particle incandescence in the near infrared along one optical path and reflected visible light along a second path. A long focal length microscope was coupled to a photoquadrocular head, modified to incorporate 40 mm diameter optical filters. The modified quadrocular head houses a beam splitter that projects identical images to two photography ports. One port is equipped with a Schott red glass filter that passes wavelengths greater than 700 nm and a monochrome frame-transfer CCD camera connected to a digital image acquisition system. The video images from this port are the result of particle incandescence from 700 nm to about 1000 nm, the long-wavelength cutoff of CCD chip sensitivity. The brightness of these images is related to particle temperature and thus to combustion rate, and the images will provide useful information on single-particle combustion and extinction behavior. It is planned to calibrate the system with a high-temperature black-body source, modified to accommodate microscope optics. The calibration may allow quantitative interpretation of the brightness levels.

A color CCD camera is attached to the second port to image visible light, supplied by a fiber-optic illuminator and reflected from char particle surfaces. These images are useful for tracking detailed changes in particle morphology, including the transition from carbon-rich to inorganic-rich particles with the concomitant changes in reflectance properties. A complete description of the experiment will be presented with the first set of results in the next quarterly report.

SUBTASK 1.2 CHAR COMBUSTION KINETICS TO HIGH CARBON CONVERSION

This quarter, the properties of the carbonaceous matrix of coal chars were characterized as a function of extent of combustion. This work is part of an effort, initiated last quarter, to explain the loss of reactivity and early extinction observed at high conversion for a variety of coal chars described in previous reports (Hurt and Hardesty, 1992a,b; Hurt et al., 1993). Numerous sets of partially-reacted chars were examined over the course of this study, including six sets from PETC-suite coals (Illinois #6, Pittsburgh #8, Lower Kittanning, Pocahontas #3, Dietz, and Beulah lignite) and two sets from Lower Freeport and Eagle seam bituminous coals, for which proximate analyses appear in Table 1.1. A sequence of partially-reacted chars from Illinois #6, PSOC-1493 were characterized in the most detail.

Mechanisms Leading to Low Reactivity at High Conversion

Low combustion reactivities have been documented for a variety of highly-reacted coal chars, as described in previous reports and articles (Hurt and Hardesty, 1992b,c; Hurt et al.,

Table 1.1
Proximate Analyses of Parent Coals
Used in Surface Area Determinations*

	<i>Lower Freeport</i>	<i>Eagle</i>
Moisture	4.85	3.81
Volatile Matter	24.9	33.94
Fixed Carbon	60.62	57.24
Ash	9.63	5.01

* Proximate and elemental analyses of PETC-suite coals are found in Mitchell et al., (1992)

1993a,b). The goal of the present research is to understand the underlying physical and chemical phenomena responsible for the low reactivities. These phenomena can be classified into three groups related to: 1) changes in particle morphology and their effect on surface area accessibility; 2) interactions between the carbon and the inorganic material; and 3) carbon structural changes on the atomic or mesoscale leading to changes in surface area or available reaction sites. Many aspects of the first two factors were treated in the previous report (Hurt et al., 1993). This report focuses primarily on the last factor, carbon structural changes, but also treats the issue of carbon availability, which logically belongs under particle morphology or carbon/mineral interactions.

There is an extensive literature on the crystalline structure of carbon materials but very little information on structural evolution under combustion conditions (high particle temperatures, 1400 - 2400 K, short times, < 1 sec, and oxidative conditions. Potentially useful techniques include X-ray diffraction, Raman spectroscopy, optical reflectance and bireflectance (Johnson, 1986) and high resolution transmission electron microscopy, (HRTEM). Because of the very limited data, there is no comparative evaluation of the techniques for characterizing carbon structural changes during combustion. Here we will examine reflectance, HRTEM, and XRD, and will demonstrate the great potential of HRTEM for coal char combustion studies.

First, the fundamental equations describing reaction and diffusion in porous char particles will be examined in order to identify the fundamental properties that determine the measured global reactivities. Then we will characterize, as completely as we can, how these properties evolve over the course of the combustion process. Finally conclusions are drawn about the likely cause of the low reactivities and the near-extinction phenomena observed at high conversion.

Theory: The Fundamental Components of Global Reactivity

This section contains a theoretical treatment of the fundamental reaction and diffusion process that determine global reactivity, with the ultimate goal of explaining the previously observed low reactivities at high conversion (Hurt, 1993; Hurt et al., 1993). The global reactivity, r_g , of porous char particles is defined here as a burning rate per unit external surface area in a specified combustion environment at a specified particle temperature. The global reactivity, r_g , with units g-carbon/s-cm²-external surface, can be expressed in terms of fundamental char properties as:

$$r_g = q_i S (m_c / V_p) \eta / (4\pi R_p^2) \quad (1.1)$$

where q_i is the intrinsic reaction rate per unit internal surface area (g-carbon/s-cm²-internal surface), S is the internal surface area (m²/g-carbon), m_c / V_p is the mass of carbonaceous solid per unit particle volume (g-carbon/cm³), η is the effectiveness factor accounting for pore diffusion effects, and R_p is the char particle radius. This formulation assumes a homogeneous and isothermal spherical particle. We assume for sake of this analysis that the intrinsic surface kinetics are described by simple, first-order kinetics, according to:

$$q_i = k_i P_s \quad (1.2)$$

where k_i is the intrinsic reaction rate coefficient and P_s is the oxygen partial pressure at the external surface of the particle. For large diffusional resistances (zone II combustion) the effectiveness factor can be written in terms of the Thiele modulus (ϕ) as follows (Froment and Bishoff, 1979):

$$\eta = 3 / \phi \quad (1.3)$$

with the Thiele modulus defined to be:

$$\phi = R_p \sqrt{\frac{k_v}{D_{eff}}} \quad (1.4)$$

In Eq. 1.4, k_v is the volumetric rate constant, given by:

$$k_v = k_i S (m_c / V_p) \nu \quad (1.5)$$

where ν is a stoichiometric factor and D_{eff} is the effective diffusivity in porous media, given by

$$D_{eff} = D \Theta / \tau \quad (1.6)$$

where Θ is the porosity and τ is the empirical tortuosity factor (Satterfield, 1981). Combining Eqs. 1.1 through 1.6 yields for the global reactivity:

$$r_g = (3/4\pi) (P_s / R_p) (S)^{1/2} (k_i / \nu)^{1/2} (m_c / V_p)^{1/2} (D \Theta / \tau)^{1/2} \quad (1.7)$$

For a particle of radius R_p , burning under conditions that produce a surface oxygen partial pressure P_s , the global reactivity, r_g , is determined by the following set of char properties:

$$r_g \sim (S)^{1/2} (k_i)^{1/2} (m_c / V_p)^{1/2} (D\Theta / \tau)^{1/2} \quad (1.8)$$

The parameter grouping (m_c / V_p) describes the availability of carbon mass in an ash-containing particle matrix and will be referred to as the "carbon availability". Equation 1.8 indicates that low carbon availability, such as occurs for a highly-reacted inorganic-rich particle with small carbon inclusions, will give rise to a low global reactivity. The four parameter groupings in Eq. 1.8 represent the four factors that determine global reactivity for any carbon material:

- a) the carbon availability, $(m_c / V_p)^{1/2}$
- b) the surface area of carbon per unit weight of carbon, $(S)^{1/2}$
- c) the intrinsic reactivity of the surface, $(k_i)^{1/2}$
- d) the accessibility of the surface, $(D\Theta / \tau)^{1/2}$

The parameters in Eq. 1.8 specify which chemical and physical characteristics must be examined in order to explain the observed decrease in global reactivity (Hurt and Hardesty, 1992). Several of the parameters, however, are difficult to measure directly, most notably k_i and $D\Theta / \tau$, and their measurement is the subject of ongoing research efforts (see for example Valix et al., (1992)). Nevertheless, a variety of analytical techniques are useful for obtaining qualitative and semi-quantitative insight on the role of each of these parameters.

Analytical Techniques

A variety of experimental techniques were employed to characterize the chemistry and structure of the carbonaceous char matrix of partially-reacted chars. The partially reacted chars were extracted from the CCL by a rapid-quench sampling probe at various residence times and analyzed without additional treatment, except as noted below. Illinois #6 chars at residence times longer than 117 msec were prepared by multiple capture and reinjection, whereas chars from each of the other coals were collected during the first pass only. The analytical techniques are briefly described below.

High resolution transmission electron microscopy

High resolution transmission electron microscopy (HRTEM) was applied to characterize partially-reacted char samples in collaboration with Sandians Nancy Yang and Thomas Headley, using the HRTEM facility at Sandia, New Mexico. HRTEM is capable of providing detailed information on the crystalline structure of carbon materials that are prepared in such a way as to be sufficiently thin to partially transmit the electron beam. The superior resolution of HRTEM allows one to distinguish individual graphitic layers oriented perpendicular to the image plane and to extract quantitative information on interlayer spacings in parallel groupings of layers. HRTEM images yield a wealth of information on the degree and nature of crystallinity in carbons, including the dimensions (lengths) of the

graphitic layers and the extent of parallel alignment of neighboring layers (stacking depths). Soot particles generally fulfill the requirement of optical thinness, without laborious sample preparation. Application of the technique to most other carbon samples requires the preparation of thin sections, usually accomplished by ultramicrotoming.

In the present study, optically thin regions of char particles are prepared by a simple and practical technique, in which the sample is hand-ground to a fine powder and then examined at moderate magnification to find wedge-shaped fragments that are optically thin at the edge. A number of such edge regions (typically ten or more) are then photographed at high magnifications (approximately 2,000,000 x) and representative fields of view selected and reproduced for discussion.

X-ray diffraction (XRD)

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 can also be used to reveal the degree of crystalline order in the char. The mean graphitic crystallite diameter (L_a) and stacking height (L_c) can be obtained by measurement of the broadening of appropriate peaks and the mean interlayer spacing (d_{002}) can be obtained from the angle of the (002) peak (Short and Walker, 1963).

In collaboration with Sandian Dale Boehme, X-ray diffraction spectra were obtained for several partially-reacted Illinois #6 char samples. The as-collected samples were ground by hand to a fine powder, placed on a specially prepared quartz crystal, and irradiated with Cu K_α radiation (1.5406 Å wavelength) in the XRD facility at Sandia, California. Diffraction spectra were obtained by varying incident angle and the spectral baselines corrected for amorphous scattering.

Carbon dioxide vapor adsorption

Micropore surface areas of various partially-reacted chars were determined by the Coors Analytical Laboratory, Golden, CO, by application of the Dubinin-Polanyi equation to carbon dioxide vapor adsorption isotherms. The samples were outgassed at 100 °C for approximately 16 hours prior to adsorption experiments. Because most of the surface area in coal chars lies in fine pores whose dimensions are comparable to the gaseous species involved in combustion (O_2 , CO, CO_2), the direct relevance of the absolute area values to combustion reactivity is not clearly established. The surface area values reported here are therefore primarily useful for identifying trends and revealing gross differences between samples.

Elemental analysis

Elemental hydrogen, carbon, and oxygen contents were determined for various partially-reacted char samples. Analyses were performed by Coors Analytical Laboratories on duplicate 10 - 20 mg samples. Hydrogen to carbon ratios are presented only for chars with ash contents less than 50%, and oxygen to carbon ratios are presented only for chars with

ash contents less than 30%. High ash contents were found to interfere with the accurate determination of organic carbon, hydrogen and oxygen due to the presence of volatile inorganic sources such as carbonates and hydroxides (Given and Yarzab, 1978; Hurt et al., 1993a).

Reflected light analysis

Polished cross sections of partially reacted Illinois #6 char samples was examined under reflected light by Gareth Mitchell of the Coal and Organic Petrology Laboratories of The Pennsylvania State University. Of particular interest were changes in the petrology, morphology, and reflectance of the samples during the combustion process. The Illinois #6 coal and its sequence of three partially reacted chars were selected for study. There were not sufficient quantities of the partially-reacted samples to use ASTM preparation procedures. The custom sample preparation procedure is described in the Appendix.

The work to date has focused on identifying qualitative differences among the samples. Where differences were observed, initial quantitative analyses have also been performed. The quantitative work to date includes measurements of mean random vitrinite reflectance for ~ 50 counts and a semiquantitative point count of particle morphology using the classification scheme of Bailey et al. (1991). Work is continuing to quantify the observed trends in particle morphologies and reflectances.

Thermal gravimetric analysis

The oxidation reactivity at 300 - 900 °C of selected Illinois #6 char samples is being measured by the research group of Professor Jon Gibbins of Imperial College using thermogravimetric analysis (TGA). This will provide important information on the changes in intrinsic oxidation reactivity during high temperature combustion. Initial tests have shown that a special procedure is required to measure reaction rates for the samples with high ash content. The loss of inorganic volatile matter in the form of hydroxides and carbonates can interfere with the gravimetric determination of reaction rates. A subtraction technique to correct for the inorganic portion of the weight loss is currently being evaluated.

Measurement of carbon availability

The carbon availability, defined as m_c / V_p , is directly related to global reactivity by Eq. 1.8. The change in this property with conversion will be inferred from previously reported measurements of particle density (Hurt and Hardesty, 1992a).

Results of Sample Analyses

In this section the results of the various analytical techniques are presented and their implications for char reactivity are discussed.

High resolution transmission electron microscopy (HRTEM)

Figures 1.1 - 1.3 show high-resolution transmission micrographs of a set of partially-reacted Illinois #6 chars at varying extents of conversion. The chars are prepared by injection of size classified raw coal (75 - 106 μm diameter) into the 12 mole-% oxygen environment in the CCL laminar flow reactor (nominal gas temperature 1600 K) and samples are extracted at residence times of 47, 72, and 117 msec.

The images presented were chosen to represent typical structures based on examination of at least ten fields for each sample. Individual graphitic layers are easily discernable in the images, often in a parallel grouping with the nominal interlayer spacing characteristic of graphitic carbon. The degree of order in the images appears to decrease with increasing distance from the optically thin region at the edge of the sample. In the optically thicker regions in the lower portions of the figures, images of several graphitic planes with different orientations are superimposed, giving the appearance of shorter length scales and a lower degree of order. Thicker samples are opaque to the electron beam and yield dark, featureless images. The region of interest in these images is therefore the optically thin zones near the sample edges, which are the only reliable indicators of crystalline structure. Note that these thin zones do not necessarily represent edges in the original sample, but may represent interior regions that have been exposed upon grinding during sample preparation.

Curved structures are present in both images as has been observed for other carbon materials. Indeed, there is evidence that curved structures are thermodynamically favored for graphitic carbon units below a certain size. For carbons that lack non-sp²-bonding heteroatoms, flat graphitic units of small size would imply a large fraction of high-energy, dangling edge carbons (Zhang, et al., 1986). Stable allotropes of carbon with curved structures include the celebrated fullerenes (Kroto et al., 1985) as well as larger carbon spheres (up to 47 nm in diameter) that have been shown to arise during high-energy electron bombardment of soot (Ugarte, 1992). Curved or closed structures have also been predicted for initially planar graphitic ribbons of 32 to 108 atoms heated to 1000 °C by molecular dynamics simulations (Brenner, et al., 1992).

By considering the thin regions near the sample edges in Figs. 1.1 - 1.3, we can clearly see that the degree of turbostratic crystalline order[†] increases between 47 msec and 117 msec residence time. The 47 msec sample was collected and rapidly quenched at a point

[†] The ordered regions in many carbon materials have a crystalline structure that is similar but not identical to that of graphite. The individual layers have the same structure as graphitic basal planes, and the layers are oriented parallel to one another with the approximate interlayer spacing of crystalline graphite. The layers are translated or rotated, however, in the planes in which they reside so that the carbon atoms in one plane exhibit no special orientation with respect to carbon atoms in adjacent planes. This is the so-called "turbostratic" structure of carbon materials prepared at temperatures and times less than those required for true graphite formation. The turbostratic nature of the coal chars in this study is confirmed by the X-ray diffraction spectrum presented in a subsequent section. The atomic rearrangements that lead to this increase in turbostratic order, but not to true graphitic crystallinity in the time and temperature range of interest, will be referred to as "pregraphitization."

|-----|
10 nm

Figure 1.1 High resolution transmission electron micrograph of young Illinois #6 coal char. Char sample collected at approximate end of devolatilization zone, after 47 msec of combustion in 12 mole-% oxygen at a nominal gas temperature of 1600 K.

10 nm

Figure 1.2 High resolution transmission electron micrograph of partially-reacted Illinois #6 coal char. Char sample collected after 72 msec of combustion in 12 mole-% oxygen at a nominal gas temperature of 1600 K.

Figure 1.3 High resolution transmission electron micrograph of highly-reacted Illinois #6 coal char. Char sample collected after 117 msec of combustion in 12 mole-% oxygen at a nominal gas temperature of 1600 K. Bulk char carbon conversion 76 %.

immediately following the disappearance of the visible volatile flame, yielding a very young char that has experienced very little oxidation. Figure 1.1 shows that this char is primarily amorphous, with only a few small regions of turbostratic order where parallel alignment of neighboring graphitic planes is visible.

The char sample extracted after 72 msec of combustion contains amorphous regions comparable to those seen in Fig. 1.1 as well as regions with easily discernable turbostratic structure. An example of the regions with turbostratic structure in the 72 msec char is reproduced in Fig. 1.2. In this image, the graphitic layers have lengths on the order of 2 - 10 nm. A number of parallel arrangements, or turbostratic crystallites, are observed with stacking depths of up to five layers. The crystalline structure continues to develop beyond 72 msec, resulting in the structure seen in Fig. 1.3 at 117 msec residence time. Both the number and size of identifiable crystalline regions is greater in this sample. Turbostratic crystallites of stacking depths up to 10 layers (~ 3.5 nm) are found in this field-of-view.

This image sequence indicates that the crystalline structure of chars develops during high temperature combustion over a time scale comparable to that of the heterogeneous oxidation reactions. The development of order is believed to be primarily governed by particle temperature histories, but may be enhanced by the oxidative removal of carbon atoms, as has been suggested for lower temperature oxidation (Hurt et al., 1988).

The development of crystalline order is believed to have important implications for char reactivity and the combustion process at high conversion. Although the degree of crystallinity does not appear explicitly in the expression for the global reactivity (Eq. 1.8) it is believed to affect intrinsic surface reactivity, k_i , microporous surface areas (which are the dominant contributor to total surface area, S , and possibly microporous diffusion coefficients, which may effect the overall diffusivity, D_{eff}) (Valix et al., 1992). In particular, when the dimensions of the graphitic layers increase, intrinsic reactivity, k_i , is expected to decrease as the ratio of reactive edge sites to unreactive basal plane sites decreases. This process is often accompanied by evolution of hydrogen from the edges of aromatic units, as noted in a subsequent section.

In addition to the effect on intrinsic reactivity, the development of crystalline structure is often accompanied by loss of total surface area, S . Most of the surface area in high-area carbons resides in micropores, which represent voids created by disorder in the crystalline structure (Wigmans, 1989). The atomic rearrangements that lead to crystallite growth eliminate these voids, leading either to net densification or to pore coalescence and pore coarsening (Hurt et al., 1988). In either case the total surface area tends to decrease, a trend which is seen here by direct measurement of total surface areas by vapor adsorption (see later section).

X-ray diffraction

X-ray diffraction (XRD) can be a convenient and useful technique for following the pregraphitization process of carbon, allowing, in many cases, the determination of lamellar dimensions and stacking heights. For the chars tested (Illinois #6), the interpretation of XRD spectra is complicated by the presence of amorphous carbon intermingled with

turbostratic carbon as well as amorphous and crystalline mineral matter (particularly silica and mullite). As the carbon conversion increases, the potential interference of mineral matter is amplified. Due to these effects comparisons of the chars at various residence times in the CCL reactor can not be made at this time. Information can, however, be obtained from the 47 msec residence time sample, where the inorganic content is relatively low.

Figure 1.4 displays two XRD spectra of the 47 msec char and the 234 msec char samples. The narrow peaks indicate the presence of the crystalline phases quartz, mullite, and maghemite and make quantitative analysis of the carbon peaks impossible for the 234 msec char sample. Qualitatively, both spectra contain only the two-dimensional (hk) type bands indicative of turbostratic carbons. Bands of the (hkl) type do not occur until the stacked aromatic layers begin to arrange in a three-dimensional graphitic structure. As mentioned, the crystallinity of the carbon in the char samples can be gauged in a number of different ways using an X-ray diffraction spectra. The (002) reflection, a result of the coherent Bragg scattering from the parallel planes, can be used to determine both a mean stacking height (using a Scherrer-type formula[†]) and the spacing between the aromatic layers (using Bragg's Law). The (002) peak is the largest of the graphite peaks and occurs at a diffraction angle of approximately 12 degrees ($2\theta = 24^\circ$). The (10) and (11) bands results from Bragg scattering from single aromatic layers and either or both can be used, again, with a Scherrer type formula, to determine a mean crystallite diameter. The (10) band is at 44° and the (11) band, which is not shown in Fig 1.4, is at 80° .

The X-ray diffraction spectra indicate the presence of turbostratic rather than graphitic structure in the partially-reacted coal chars. Quantitative analysis of the spectra are underway. Because of the importance of pregraphitization in char combustion, both XRD and HRTEM will be evaluated as tools for characterizing the pregraphitization process. To pursue XRD further, separation of a carbon rich portion (perhaps by density segregation or demineralization) or the use of a X-ray micro-diffractometer, which has recently become available here at Sandia, will be needed for the highly-reacted samples.

Carbon dioxide vapor adsorption

The surface areas were determined by application of the Dubinin-Polanyi equation to the carbon dioxide adsorption isotherms measured for a variety of partially-reacted chars prepared in the CCL. The areas are normalized by the weight of carbonaceous (organic) material in the samples (mineral matter has a negligible surface area by comparison) and are presented in Figures 1.5 and 1.6. To focus on the char combustion phase, conversions in

[†] Scherrer (1918) developed an expression relating the edge dimension, L, of a crystal to the X-ray diffraction line broadening, β , such that

$$L = K \frac{\lambda}{\beta \cos \theta}$$

where K is a constant of order one, λ is the wavelength of the radiation, and θ is the Bragg angle.

Figure 1.4 X-ray diffraction patterns of partially-reacted Illinois #6 chars sampled at two residence times (the baseline for the 47 msec char is an intensity of 20).

Figs. 1.5 and 1.6 are put on a volatile-free, or char, basis with the young char at 47 msec residence time defining the zero conversion point. The carbon dioxide surface areas are believed to be an approximate measure of the total surface area available for the heterogeneous oxidation reactions (Walker and Patel, 1970; Hurt et al., 1991).

Surface areas decrease rapidly in the initial phases of char combustion process, by factors of up to three between 47 and 72 msec. Beyond 72 msec, the areas decrease more gradually and, for five of the nine cases, reach a minimum and increase slightly at the longest times studied. There is also a rough correlation between the absolute values of surface area in Figs. 1.5 and 1.6 and parent coal rank, with the low rank coals exhibiting the highest areas. There is no significant systematic difference between the data in 6 and 12 mole-% oxygen.

Figure 1.5 Surface areas determined by carbon dioxide adsorption for various partially-reacted chars. Chars produced by raw coal injection in the CCL laminar flow reactor in either the 6 or 12 mole-% oxygen environment and isokinetically sampled at residence times from 47 to 117 msec.

Models that describe the widening and coalescence of pores by oxidation predict surface areas that *increase monotonically* with conversion when normalized per gram of remaining organic matter as in Figs. 1.5 and 1.6 (Gavalas, 1980, Hurt et al., 1988). The predominant downward trend in Figs. 1.5 and 1.6 cannot be predicted by considering the effect of oxidation on a rigid porous matrix, but indicates rather the affects of thermally induced lattice rearrangements, or pregraphitization. High temperature char combustion affects surface areas through the simultaneous action of heat treatment (which tends to destroy area) and oxidation (which tends to create area). In the early stages of combustion, where particle temperatures are high and carbon structure is evolving rapidly, pregraphitization is the dominant of the two competing factors and surface areas are observed to decrease sharply. Assuming the pregraphitization process to be asymptotic, at later times the effect of oxidation will become more apparent and surface areas will stop decreasing or, as seen for some chars in Figs. 1.5 and 1.6, will increase slightly.

In the late stages of char combustion in laboratory reactors or large-scale furnaces, particle temperatures are typically lower, and it is expected that further pregraphitization would be slower, that oxidation occurs more uniformly throughout the char particles and that surface

Figure 1.6 Normalized surface areas for chars in various stages of combustion. The partially oxidized chars are produced by raw coal injection in the CCL laminar flow reactor in either the 6 or 12 mole-% oxygen environment and isokinetically sampled at residence times from 47 to 117 msec.

area remains constant or perhaps increases. We have recently examined residual carbon samples in fly ash from commercial-scale coal combustion systems and have found their surface areas to be roughly comparable to the chars in Figs. 1.5 and 1.6 sampled at residence times of 72 msec or longer (Hurt et al., 1993b).

Elemental analysis

Figure 1.7 presents hydrogen to carbon weight ratios (H/C) for a variety of partially-oxidized chars sampled from the CCL entrained flow reactor at selected residence times. The H/C ratios of the raw coals vary from 5 to 7%. Hydrogen is evolved much more rapidly than carbon during devolatilization, leading to large decreases in H/C ratio between 0 and 47 msec. The H/C ratio continues to decrease significantly during the early stages of char combustion (from 47 to 72 msec) but decreases more gradually thereafter.

Figure 1.8 presents analogous information on O/C ratios for the same set of samples. Oxygen, like hydrogen, is lost more rapidly than carbon during devolatilization and early char

Figure 1.7 Hydrogen to carbon weight ratios for chars of selected coals from the PETC coal suite (Mitchell et al., 1992) at various stages of combustion. Chars produced by raw coal injection in the CCL laminar flow reactor in either the 6 or 12 mole-% oxygen environment and isokinetically sampled at residence times from 47 to 117 msec.

combustion. During the intermediate stages of char combustion (between 70 - 100 msec) O/C ratios are approximately constant or decrease slightly.

The decrease in H/C and O/C ratios are indicative of the loss of aliphatic material, the coalescence of aromatic units, and loss of reactive edge sites. Hydrogen content has been shown to correlate with char reactivity to oxygen as measured by thermogravimetry (Charpenay et al., 1992). This process can be classified either as the last stage of devolatilization or as a char maturation/pregraphitization process, depending on which aspect of the process is of interest in a particular circumstance. The term late devolatilization emphasizes the weight loss, while the terms char maturation or pregraphitization emphasize the solid state transformations. Here the term pregraphitization is used to focus on the solid transformations, which are closely related to char reactivity.

Figure 1.8 Oxygen to carbon weight ratios for chars of selected coals from the PETC coal suite (Mitchell et al., 1992) at various stages of combustion. Chars produced by raw coal injection in the CCL laminar flow reactor in either the 6 or 12 mole-% oxygen environment and isokinetically sampled at residence times from 47 to 117 msec.

Reflected light analysis

Two important observations can be made regarding the set of partially reacted Illinois #6 chars. First, the mean random vitrinite reflectance increases with increasing degree of conversion as seen in Table 1. Increases in reflectance have been observed with increasing severity of pyrolysis (Goodarzi and Murchison, 1972; Chandra and Bond, 1956), and have been attributed to increases in aromaticity and degree of crystalline order (Murchison, 1978). Other authors (Johnson et al., 1986, Goodarzi, 1984) have shown that reflectance increases monotonically with heat treatment temperature from 400 - 1000 °C, but decreases slightly at higher temperatures. These same authors claim that Raman spectra contain enough information to infer heat treatment temperature within 100 °C between 500 - 1900 °C for a range of coal chars. These studies all involve heat treatment time scales on the order of hours and not milliseconds as in the present work. The increase in reflectance from 47 to 117 msec is likely related to the increase in molecular order seen in the HRTEM analyses.

Secondly, the fraction of particles with characteristic inertinite morphologies increases with conversion. The particle morphology classification scheme of Bailey et al. (1990) includes three particle types (inertoid, solid, and fusinoid) commonly derived from the inert (nonfusible) components of coal. In the present study, the fraction of these inertinite-derived char particles is observed to increase from approximately 6 vol-% in the young, unoxidized Illinois #6 char at 47 msec residence time, to 18 vol-% after 117 msec residence time and 25 vol-% after 234 msec. The enrichment of inertinite-derived particle types at high conversion indicates longer average burnout times for inertinite-derived chars.

Total burnout time is a strong function of both reactivity and initial char particle density. The inertinite-derived char types are characterized by a higher density (lower macroporosity) than the vitrinite-derived types (Bailey, et al., 1990). Inertinite-derived chars have also been observed to be less reactive than vitrinite-derived chars or chars from whole coals by a

Table 1.2
Mean Random Vitrinite Reflectance
of Partially-Reacted Illinois #6 Chars

<i>Combustion residence time (msec)</i>	<i>Char carbon conversion (%)</i>	<i>Mean random vitrinite reflectance (%)</i>	<i>90% confidence limits on mean (%)</i>
47	0	6.38	+/- 0.3
117	76	6.91	+/- 0.18
234	90	7.48	+/- 0.32

number of researchers. An inertinite-rich maceral fraction was found by Wall, et al. (1992) to burn at approximately half the rate of a vitrinite-rich fraction under similar conditions to those used in the present study, and to have characteristic burn-out times that are a factor of three to four longer.

The enrichment of inertinite-derived char particles is therefore due to a combination of their generally lower reactivities and higher densities. Inertinite enrichment contributes to the low reactivities observed at high conversion, but the degree of enrichment and the reactivity differences between inertinite and vitrinite-derived chars are not large enough, alone, to explain the observed loss of reactivity at high conversion (Hurt and Hardesty, 1992, Hurt et al., 1993).

Measurement of carbon availability

The carbon availability, or mass of carbon per unit particle volume, m_c / V_p , is directly related to global reactivity by Eq. 1.8. The change in this property with conversion can be treated using previously reported particle density measurements and the model proposed by Mitchell et al. (1992). The model expresses the reciprocal particle density as the sum of two terms:

$$1/\rho = V_p/m_p = x_a/\rho_a + (1-x_a)/\rho_c \quad (1.9)$$

where x_a is the weight fraction ash in the particle, ρ_a is the ash density, and ρ_c is the density of the porous carbon matrix. The change in carbon density, ρ_c , with conversion has been described by an empirical relation of the form:

$$\rho_c = \rho_{c_0}(1-X)^\alpha \quad (1.10)$$

where α is the empirical mode of burning parameter, taking values from 0 (constant density burning) to 1 (shrinking core behavior). Values of α have been determined for 100 μm diameter char particle from a range of coals (Hurt and Mitchell, 1992) and vary from 0 to 0.3, with a mean value of approximately 0.2. In terms of this model, the carbon availability, m_c / V_p can be expressed as:

$$m_c / V_p = \rho (m_c / m_p) = \rho (1 - x_a) \quad (1.11)$$

combining equations 1.9 - 1.11 yields:

$$\frac{m_c}{V_p} = \frac{1}{\frac{1}{\rho_{c_0}(1-X)^\alpha} + \frac{x_a}{(1-x_a)\rho_a}} \quad (1.12)$$

where the ash content is related to the initial ash content, x_{a_0} , and the degree of conversion:

$$x_a = \frac{1}{1 + \left[\frac{(1-x_{a_0})}{x_{a_0}} (1-X) \right]} \quad (1.13)$$

Equation 1.12 is used to plot the changes in carbon availability with conversion in Fig. 1.9 for typical values of ρ_{c_0} (0.5 g/cm³) and ρ_a (2 g/cm³) and for various values of α and the initial ash content, x_{a_0} . Loss of carbon availability is seen to reduce particle global reactivity to an extent that depends on the degree of internal burning (represented by α) and the initial ash content. Carbon availability reduces global reactivity primarily late in combustion, at char carbon conversions greater than 80% to 90%. High ash contents reduce carbon availability through "dilution" of the carbon mass in a primarily inorganic matrix. At very high conversions ($X > 98\%$) this dilution effect is large enough that it alone (without considering loss of reactivity by the other mechanisms discussed here) is sufficient to cause certain near-extinction of the ash-rich particles. Because the near extinction occurs earlier than this for Illinois #6 (Hurt and Hardesty, 1992), and has been directly observed for very low ash

Fig. 1.9 Square root of normalized carbon availability as a function of extent of char carbon conversion for typical char and ash properties.

content particles through captive particle imaging, effects other than carbon availability must also contribute to the global reactivity loss, such as pregraphitization.

Note that this analysis assumes a homogeneous particle with the residual carbon well dispersed in the inorganic matrix. Similar but quantitatively different results are obtained if the carbon is located preferentially in the particle interior, surrounded by an outer porous ash layer.

Conclusions

This report combined with the previous quarterly report (Hurt et al., 1993) offer an extensive characterization of partially-reacted Illinois #6 chars and additional characterization of partially-reacted chars from a variety of other coals. These analyses identify three primary factors that combine to make coal chars progressively less reactive as the process of high temperature combustion proceeds. The three factors are:

- 1) Evolution of the organic molecular structure. The composition and crystalline structure of the carbonaceous organic matrix evolves during the char oxidation phase. Atomic-scale rearrangements are observed to occur in the first 70 msec of the char combustion phase (between 47 and 117 msec total residence time) leading to a gradual loss of hydrogen, coalescence of aromatic structures, and turbostratic crystallite growth. This

pregraphitization brings about loss of microporous surface area and a likely reduction in the intrinsic reactivity of the surfaces.

- 2) Loss of carbon availability. Carbon availability, expressed as m_c / V_p , with units of grams of carbon per unit particle volume, decreases as carbon atoms are consumed by oxidation. This effect is only modest at low-to-intermediate conversions or for low ash content materials, but can become quite significant for high ash content materials at high conversion (>90%). At very high conversion, residual carbon can occur primarily as inclusions in coherent inorganic frameworks. Such particles have very low carbon availabilities and thus very low global reactivities.
- 3) Low reactivity particles or subparticle regions present in the young char, at least some of which are derived from inertinite-rich coal particles, become enriched in the highly reacted residue due to their longer burnout times. Inertinite enrichment contributes to low reactivities at high conversion, but cannot, alone, explain the near-extinction phenomena, as the degree of enrichment and the reactivity differences between inertinite and vitrinite-derived chars are typically not large enough.

The loss of reactivity by factor (1) is primarily governed by the temperature history of the char particles, while factors (2) and (3) are primarily governed by the extent of oxidation. Further work is necessary to quantify the relative importance of these three factors, and to formulate time and conversion-dependent kinetic models to account for them.

NOMENCLATURE FOR TASK 1

d_{002}	interlayer spacing, spacing between graphitic basal planes, nm
d_p	particle diameter, cm
D	diffusivity, $\text{cm}^2 \text{sec}^{-1}$
D_{eff}	effective pore diffusivity, $\text{cm}^2 \text{sec}^{-1}$
k_i	intrinsic surface rate constant, $\text{g-C cm}^{-2} \text{s}^{-1} \text{atm}^{-n}$
k_v	volumetric rate constant, $\text{mol O}_2/\text{cm}^3\text{-s}-(\text{mol/lit})^{n_i}$
K	constant in the Scherrer equation
L_a	carbon crystallite dimension in graphitic basal plane, nm
L_c	carbon crystallite dimension normal to graphitic basal plane, nm
m_c	mass of carbonaceous (combustible) material in ash-containing particle
P_s	oxygen partial pressure at the particle surface, atm
q_i	intrinsic surface oxidation rate, $\text{g-C s}^{-1} \text{cm}^{-2}$ -internal surface
r_g	global particle reactivity, or overall particle burning rate per unit external
R_p	particle radius
S	internal surface area per unit mass of organic material, m^2/g
T_g	gas temperature, K
T_p	particle temperature, K
V_p	particle volume, cm^3
x_a	weight fraction ash
X	char carbon conversion

Greek symbols

α	mode of burning parameter
β	X-ray diffraction line width
η	effectiveness factor
ϕ	Thiele modulus
θ	Bragg angle
Θ	porosity
ρ	char particle density, g/cm ³
ρ_a	ash density, g/cm ³
ρ_c	porous carbon density, g/cm ³
ν	stoichiometric factor, moles oxygen/g-carbon

Other

subscript "o" indicates a property of the young, unoxidized char, sampled after 47 msec residence time

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PLANS FOR NEXT QUARTER

The insights obtained this quarter on the mechanisms of reactivity loss will be used to design auxiliary experiments and/or analyses to quantitatively characterize each of the three critical factors. These experiments will provide the data necessary for formulating an advanced, conversion-dependent kinetic model.

Also next quarter, the new captive particle imaging technique will be applied to chars from Illinois #6 coal and one low rank coal to be chosen. This work should provide critical information on extinction mechanisms and the effects of coal heterogeneity.

Finally, a heated chimney is being constructed to greatly extend the residence times available in a single pass in the CCL. Extractive sampling will be performed with the heated chimney to determine weight loss profiles for Illinois #6 for comparison to those determined by multiple capture and reinjection.

PUBLICATIONS AND PRESENTATIONS

This quarter, a paper on PETC and EPRI-funded research was accepted for presentation at the Seventh International Conference on Coal Science, to be held in Banff, Alberta in September 1993. A paper was also submitted for the 1993 PETC Contractor's Conference to be held in Pittsburgh in July 1993, and an abstract was accepted for the Pittsburgh Coal Conference in September 1993. Also this quarter, the paper presented at the Annual ACERC Review Meeting on PETC-sponsored work on unburned carbon was submitted to the *Journal Energy and Fuels*. The article is entitled "Reactivity Distributions and Extinction Phenomena in Coal Char Combustion."

COLLABORATIONS, VISITORS, CONTRIBUTING PERSONNEL

This quarter, the collaboration with Professor Jon Gibbins continued and contact was made with Gareth Mitchell of the Coal and Organic Petrology Laboratories of The Pennsylvania State University. Gary Mitchell has provided valuable expertise in coal petrology and quantitative reflected light analyses. Finally, Richard Yee will be returning to the CRF this summer to work in the Coal Combustion Laboratory, with an emphasis on captive-particle imaging. Richard is a freshman at the University of California, Davis, and has almost a year of experience in the CCL through a previous high-school work/study program.

APPENDIX

Sample preparation procedure for reflected light analyses

Pulverized coal and char samples were mixed with a cold-setting epoxy resin in a 3 cm x 0.9 cm glass vial, which was first sprayed with a releasing agent. Enough epoxy was added to make a fluid mixture, but not so much as to exceed a height of 1.5 cm in the vial. The mixture was stirred to thoroughly wet the particles. The samples were then placed under vacuum to impregnate the epoxy into the porous char particles. The vials were placed in a centrifuge rotated at approximately 2000 rpm for 5 min to remove air bubbles and to produce a particle density gradient within the mixture. Samples were cured overnight under ambient conditions, after which the glass vials were broken to reveal a 1.5 x 0.9 cm cylindrical preparation. Each of these cylinders were cut in two pieces longitudinally, and the cut surface was glued face down in a 2.5 cm diameter cylindrical steel mold. Fresh epoxy was poured into the molds to complete the preparation of each sample.

Polishing was performed using a Buehler Automet polishing system. Samples were rough ground on a belt sander and then ground and polished using a succession of grit papers (400 and 600 silicon carbide) and alumina polishing compounds (0.3 μm alumina on a medium nap cloth and 0.05 μm alumina on silk). All samples were inspected using a Zeiss Axiophot research microscope at 500x magnification in reflected, white-light illumination and oil immersion.

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)

Subtask	FY92	FY93	FY94
	O N D J F M A M J J A S	O N D J F M A M J J A S	O N D J F M A M J J A S
1. High carbon conversion	1a 1b	1c 1d	1e 1f 1g 1h
2. Kinetics of heterogeneous particle populations	2a 2b	2c 2d 2e 2f	2g
3. Char formation process; effect of particle structure	3a 3b	3c 3d 3e	3f
4. Data unification	4a 4b 4c 4d		

(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: April 1, 1993 - June 30, 1993

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

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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

During the last quarter, a project plan detailing work to be performed over the next four years under this contract was submitted to PETC under separate cover. Technical progress under the existing project plan is discussed below by subtask.

SUBTASK 2.1 TRANSFORMATIONS: RELEASE OF INORGANIC MATERIAL DURING COAL COMBUSTION

Preparation of final manuscripts describing these projects is underway and will be completed in the next quarter.

SUBTASK 2.2 THE EVOLUTION OF PARTICLE AND FLY ASH SIZE DISTRIBUTIONS

All data collection and analysis for this subtask is complete. Final manuscripts describing the results are under preparation.

SUBTASK 2.3 SPECTROSCOPIC STUDIES OF INORGANIC PHASES

Introduction

Elemental composition of ash deposits can be reliably measured by collecting samples and submitting them to laboratories applying standard analytical techniques such as atomic absorption spectroscopy. This elemental chemical composition has served as one of the quantitative benchmarks for many analyses of ash deposition. If deposits are in chemical equilibrium and their temperature and morphology are known, the elemental species composition allows (in principle) a complete specification of their properties. Therefore, it is a logical point of departure for describing the chemistry of deposits. However, deposits generally are not in chemical equilibrium and important chemical reactions between the deposit and the combustion gas, between the deposit and the heat transfer surface, and between the material within the deposit itself affect the deposit properties. Two deposits with identical elemental composition may have measurably different properties because of their differing chemical species compositions. There is, therefore, a need to develop a diagnostic capable of monitoring chemical species composition of inorganic material in ash deposits.

Chemical species composition of ash deposits, unlike elemental composition, is sensitive to temperature and environment changes. Many species undergo either phase changes or chemical transformations as deposits cool if they are removed from the combustion environment to perform chemical analysis. There is, therefore, a great need for *in situ*, real-time measurements of deposit surface composition.

Both *in situ* and real-time characteristics of the diagnostics are important. The *in situ* characteristics are important for reasons mentioned above. Real-time data will allow the progress of reactions such as sulfation, oxidation, and phase transformations to be monitored. These reactions are likely to occur on both the relatively cool heat transfer surface and on the relatively hot particles in the gas phase. Sulfation of alkali and alkaline earth metals, which is one of the more significant reactions with respect to deposit formation, occurs almost exclusively on the heat transfer surfaces since most of the sulfates are not stable at combustion gas and fly ash temperatures. Sulfation reactions are implicated in the formation of tightly bound (tenacious) ash deposits.

This optical, *in situ*, real-time technique, when combined with the MFC and deposition probes, provides a unique capability to explore the chemical species transformations that occur in an ash deposit during combustion. This is one of the goals of the ash deposition work at Sandia during FY92.

Fourier transform infrared (FTIR) spectroscopy is useful for recording species-specific spectral features of organic and inorganic phases over a broad spectral range. The diagnostic technique described here involves application of FTIR spectroscopy to identification of chemical species on heat transfer surfaces in combustion environments. Radiation emitted from the deposit surface is spectrally resolved with the interferometer. The resulting spectra are used to identify the chemical species in the diagnostic area. The spectra are sensitive to temperature, thickness of the deposit, and chemical composition. Therefore, information on all three of these properties may be obtained

by proper data analysis. The technique of emission FTIR is discussed in several standard texts [Bates, 1978; Griffiths and de Haseth, 1986; Urban and Koenig, 1990], and the challenges associated with applying it as a diagnostic have been discussed in detail elsewhere [Baraldi and Fabbri, 1983]. The spectral manipulation and analysis presented below is simplified due to limitations of some of the optical and computational resources currently available on our system. However, it is sufficient to reveal the utility of the technique. More refined analyses of data will be presented after we install a mirror-based optical system and upgrade the computational resources of the FTIR.

Progress during FY92 in demonstrating this FTIR technique for application to a heat transfer surface in particle-laden, reacting flows is summarized below. Included are discussions in two major areas; (1) instrumentation and design modifications and (2) proof of concept experiments demonstrating the technique as an *in situ*, real-time diagnostic for coal ash deposits in flows in Sandia's Multifuel Combustor, a pilot-scale coal combustion facility. These topics will be discussed in the following two subsections.

Fuels, Equipment, and Experimental Design

Fuels

Chemical and combustion analyses of the coals used in this investigation are indicated in Table 2.1. Spectra from the Wyodak coal and the blend are discussed later. The Wyodak coal is a typical Powder River Basin (PRB) coal, with slightly lower than average sodium content. Some distinguishing characteristics of the PRB coals relative to the high-volatile bituminous coals include moderate moisture, low ash, high calcium in ash, and low iron in ash. The Eagle Butte coal is a similar PRB coal of somewhat lower quality, with higher alkali and alkaline earth metal content, higher moisture, slightly higher ash, high oxygen content, and lower heating value. The Kentucky #9 coal is a typical high-volatile bituminous coal from the midwestern US. Relative to the two PRB coals, it has low moisture, high heating value, high iron, low calcium, and high ash. The blend of Eagle Butte and Kentucky #9 coals is a nominal 50:50 mass mixture of the coals. Coals were blended *after* pulverization. In general, the properties of the blend are consistent with the blend ratio, although there are some exceptions. The carbon and heating value are not consistent with the blend ratio, reflecting sample-to-sample variations in coal quality.

The angular position of the probe is digitally monitored and controlled. To minimize damage to the thermocouple leads, the probe is rotated twice in alternating directions. The probe can return to any specified angular position (within a fraction of a degree of arc) after an arbitrary number of rotations. This allows spectra to be collected either from the same location on the probe at successive times, ensuring that differences in spectra represent changes on the surface rather than spatial inhomogeneities, or from many locations around the surface, to obtain averaged data. Typically, the same diagnostic area is used for every scan and it corresponds to the immediate vicinity of one of the surface thermocouples.

Table 2.1 Chemical and combustion properties of the fuels and the blend used in the combustion tests.

	<i>Wyodak</i>	<i>Eagle Butte</i>	<i>Kentucky #9</i>	<i>Eagle Butte / Kent.#9 Blend</i>
H ₂ O (mass %)	20.5	23.09	7.86	21.36
Ash (mass %, dry)	6.23	6.38	15.68	9.57
Ultimate Analysis (mass %, dry basis)				
C	69.76	66.89	64.85	68.32
H	4.95	4.89	4.60	4.76
O	17.49	20.20	9.26	14.50
N	0.97	1.17	1.61	1.11
S	0.56	0.47	4.00	1.74
Cl	0.043	0.025	0.056	
Proximate Analysis (mass %, dry basis)				
Fixed Carbon	48.27	47.95	46.77	46.53
Volatile Matter	45.50	45.67	37.56	43.90
Ash Chemistry (% of Ash)				
SiO ₂	26.07	27.91	45.70	30.83
Al ₂ O ₃	13.78	14.14	19.65	14.52
TiO ₂	1.26	0.83	0.98	0.95
Fe ₂ O ₃	5.15	6.05	23.05	14.52
CaO	23.81	25.17	3.24	13.69
MgO	4.08	5.94	1.05	3.17
K ₂ O	0.18	0.27	2.47	1.20
Na ₂ O	0.80	1.83	0.86	1.20
SO ₃	21.98	16.49	3.75	20.06
P ₂ O ₅	0.96	0.67	0.14	0.27
undetr. Ash	1.93	0.70	-0.89	-0.41
Total	100	100	100	100
Forms of Sulfur (mass % of dry fuel)				
Sulfatic	0.04	0.01	0.409	0.310
Pyritic	0.12	0.06	1.70	0.55
Organic	0.40	0.40	1.89	0.88
HHV (dry basis) [Btu/lb]	11927	11516	11611	11876

An in-line air heater (maximum heater temperature $\approx 1000\text{ }^{\circ}\text{C}$) is used to control probe surface temperature over a broader range than is achievable by room temperature air alone. Probe surface temperatures vary from 250 to 650 $^{\circ}\text{C}$, consistent with the variation common to conventional boilers. Probes of both carbon and stainless steels are used in the experiments. Ceramic probes have also been used, although they have not included the temperature monitoring and control mechanisms incorporated in the steel probes.

Emission from the surface is collected by the interferometer either with the probe stationary and, after collecting the interferograms, restarting the probe or with the probe continuously rotating. Typically, 256 duplicate interferograms are analyzed and combined to form a single spectrum. During the approximately three minutes required to collect the interferograms, the probe surface temperature typically drops by a few degrees in the region of the measurement since it is no longer exposed to radiation from the furnace. This temperature change can be compensated for by adjusting the gas flow through the tube, but the adjustments are difficult to perform with precision.

The Multifuel Combustor

All tests were conducted in the Multifuel Combustor, which has been described in detail in previous reports and, less detail, in the literature [Baxter, 1992; Baxter, 1993; Baxter and Dora, 1992; Baxter, et al., 1993].

Probe Design

During the last quarter, new stainless steel probes (water wall and tube in cross flow) were designed, built, and installed in the MFC. The new probes were built because the old carbon steel probes had been significantly damaged by ash deposits and were becoming increasingly difficult to clean after use, even using an emery cloth. We also wanted to perform higher temperature experiments and had concerns about raising carbon steel to temperatures above 550 $^{\circ}\text{C}$. Finally, we incorporated some new features in the probes, such as an in-line heater (discussed below), to provide greater flexibility in controlling probe surface temperature. The overall design features of the probe are discussed here, many of which have been discussed in the past.

The spectra discussed below are all derived from a temperature-regulated cylinder placed in cross flow in the test section of the MFC. The design and operation of this probe includes several features that are critical to the experiment.

The MFC simulates the local environment commonly experienced by a coal particle as it travels through a commercial-scale combustor, and simultaneously provides sufficient control of, and access to, the reacting stream to perform scientific measurements. One of the problems confronting emission FTIR spectroscopy as a surface diagnostic technique is differentiating furnace radiation reflected by the deposit surface from radiation being emitted by the surface. We have minimized this difficulty in the MFC by rotating the probe as it is exposed to the gas stream, generating deposits with radially uniform composition, and confining the diagnostic area to the bottom surface of the tube (see Fig. 2.1). The radiation emitted from this shadowed surface has no component derived from first-order reflection of furnace radiation. Secondary and higher order reflections from surrounding surfaces are minimized by moving surfaces as far away from the

diagnostic volume as possible. The test section is largely open to the room. Absorbing coatings are applied to the surfaces close to the area and they are maintained at low temperatures compared to the probe and the gases. The probe is thermocouple instrumented to provide temperatures of the surface at four locations and temperature changes of the air cooling fluid across the center section of the probe. The spectra collected under these conditions can be used to determine surface composition, temperature, and possibly deposit thickness.

Figure 2.1. Schematic diagram of a deposition probe designed for use in the MFC. Note that nominally uniform deposits are grown on all sides of the probe by rotating it in the flow, allowing spectra to be collected from the bottom shadowed surface.

Optics

Two optical systems have been used during the last fiscal year to collect radiation from the deposition probe. Only modest changes to these systems have been made in the last quarter. They are both discussed below, with emphasis on the earlier system no longer in use. Most of the data discussed later was originally collected with this earlier optical system. During the last quarter, it has been reanalyzed with the new algorithms to determine the extent to which the original interpretations may have been influenced by gas-phase interference in the spectra.

The earlier optical layout is shown in plan view in Figure 2.2. Two thallium bromoiodide (KRS-5) lenses are used to collect the signal from the probe and introduce it into the FTIR. These lenses are designed to minimize chromatic aberrations when working with a broad range of wavelengths. The collection lens is protected from the gases and (especially) particles of the combustion flow by

Figure 2.2. Optical layout of the FTIR experiment for measuring deposit species composition on tubes in cross flow.

an air purge incorporated around its mount. Between measurements it is protected by physical barriers. Its focal length is 10 inches. The focusing lens is actually mounted inside the FTIR on adjustable mounts and is in a nitrogen purged environment.

The spot size of the diagnostic area is controlled by an adjustable aperture installed in the FTIR housing (not shown in the figure) and ranges from approximately 1 to 5 mm, depending on aperture settings. The depth of the deposit that contributes to the emission is strongly dependent on the material optical properties. It varies from several multiples of the wavelength of the radiation in weakly absorbing regions to a fraction of a wavelength in strongly emitting regions. A typical depth is on the order of 20 microns, which is comparable to the surface roughness scale.

Improved optical performance (stronger signal, same noise) is achieved with a series of off-axis paraboloidal mirrors. The system consists of a collection mirror that collimates the signal from a point on the probe surface and a focusing mirror that focuses the light on a computer-controlled aperture added to the instrument. The primary advantages of the mirrors include: (1) improved signal-to-noise ratios; (2) longer stand-off distance for the first optical component; and (3) elimination of chromatic aberrations at instrument aperture. The effective f -number of the focusing mirror (≈ 1.8) is less than that of the instrument (≈ 1.9). The total solid angle of radiation collected in the mirror system also exceeds the solid angle collected with the lenses. This optical design increases total signal without increasing noise. The collection mirror has an effective focal length of slightly over 38 cm (15 in.), allowing it to be located further from the particle-laden vitiated flow than was possible with available KRS-5 lenses. The mirror system also eliminates chromatic aberrations that occur in lens systems. In practice, both the signal-to-noise ratio and the chromatic aberrations were tolerable in the lens system. The overwhelming motivation for changing optical designs is the damage inflicted on the collection lens by occasional hot particles landing on its surface.

FTIR Spectrometer

Only modest changes in the spectrometer were made in the last quarter. The currently used commercial system and its modifications are summarized here. A Biorad/Digilab FTS-60 Fourier transform infrared (FTIR) interferometer is used to collect the spectra. Several in-house modifications to the FTIR are required to successfully monitor surface composition. Optical modifications include replacement of the internal source and aperture of the FTIR by a turning mirror and computer-controlled aperture to accommodate the emission signal. Electronic modifications include signal conditioning of the detector output. The passage of burning particles through the optical path and the turbulent fluctuations of the gases in this path introduce strong perturbations in the collected signal that both add noise and can overwhelm the controller and A/D converters of the instrument. This problem is addressed by conditioning the signals with a high-pass, Butterworth electronic filter (cut-off frequency = 200 Hz) between the broad-band, mercury-cadmium-telluride (MCT) detector and the A/D board.

Changes to the system made during the last quarter include installation of a flipper mirror. The conceptual function of the mirror is illustrated in Fig. 2.2. The mirror allows the source of the radiation to be changed from the deposition probe to the blackbody. It can be controlled either manually or by the FTIR data station. Although Fig. 2.2 illustrates an optical system using KRS-5 lenses, our current system uses off-axis paraboloidal mirrors.

Spectral Resolution

Spectra typically are collected with a resolution of 2 cm^{-1} . This resolution allows us to distinguish gas phase radiation, principally from H_2O , CO_2 , and CO , from condensed phase radiation. The former has an inherent peak width of approximately 0.05 cm^{-1} at the gas temperatures in which we are performing experiments (1000-1800 K). Condensed phase material has peak widths of at least 8 cm^{-1} , often much larger, under the same conditions. As spectra are collected at lower resolution,

the time required to collect a given spectra, noise in the spectra, and computer storage all decrease. However, collecting spectra at insufficient resolution would preclude getting clear indications of whether some peaks originate in the gas or from the surface. We find an optimal resolution to be 2-4 cm⁻¹ and have collected all of our data at resolutions of at least 2 cm⁻¹. In regions where gas-phase lines are closely spaced, increasing the resolution increases the ease with which the gas emission lines can be distinguished from those of the condensed phase. Much of our data is collected with resolution of 0.5 cm⁻¹ for this reason. The mathematical methods used to separate gas- and condensed-phase spectral information are discussed later.

Data Analysis

The signal recorded by the MCT detector includes four terms: (1) a time-varying component generated by the interferometer and related to the spectrum of the radiation; (2) a time-varying contribution related to amplitude fluctuations of the radiation introduced into the interferometer; (3) an essentially time-invariant contribution from the walls and optical surfaces in the interferometer; and (4) noise. The sum of these components represents the measured interferogram. The component generated by the interferometer is related to the Fourier transform of the spectral sum of the radiation introduced into the instrument through the collection optics and that emitted by the optical components of the instrument between the collection optic and the beam splitter, inclusively. A portion of this signal originates from the surface, and it is this portion that we seek to analyze. Standard fast Fourier transform techniques are used to invert the interferogram and produce a spectrum. No apodization or zero-filling is used in producing the resulting single-beam spectrum. This single-beam spectrum can be expressed as

$$S(\bar{\nu}, T) = I(\bar{\nu}) [\epsilon_s(\bar{\nu}, T_s) P(\bar{\nu}, T_s) + G(\bar{\nu}, T) + O(\bar{\nu}, T)] + B(\bar{\nu}, T_i) + N(\bar{\nu}) \quad (2.1)$$

where S represents the single-beam spectrum, $\bar{\nu}$ represents wavenumber, T represents temperature, I represents an instrument response function, ϵ represents the surface emittance, P represents Planck's equation for blackbody radiation, G represents signals from gas-phase species, O represents radiation from other sources that passes through the interferometer, B represents background radiation from optical components, instrument walls, etc. that does not pass through the interferometer, and N represents noise. Subscripts on temperature indicate surface (s) and instrument (i). The temperature dependence of G is more complex, including all temperatures between peak gas temperature and room temperature. Contributions to the signal represented by O include mirror surfaces, instrument walls, furnace radiation, radiation scattered or emitted by entrained particles, room lights, and similar spurious sources. The remaining terms are quite specific and self explanatory.

Chemical species identification on the surface relies on measuring the wavenumber variation of the surface radiance. Careful analysis of the data can result in quantitative spectral emissivities, as indicated by Eq. 2.1, and each of the terms in the equation is discussed in more detail below in pursuit of this objective.

The Planck equation, P , is given by

$$P(\bar{\nu}, T) = \frac{2hc^2\bar{\nu}^3}{\exp\left(\frac{hc\bar{\nu}}{kT}\right) - 1} \quad (2.2)$$

where P is the spectral energy density at wavenumber $\bar{\nu}$, h is the Planck constant, c is the speed of light in vacuum, k is the Boltzman constant, and T is absolute temperature. The function represents the amount of radiant energy emitted from a blackbody per unit wavenumber, area, and steradian.

During this quarter, instrument response functions and background contributions have been calculated by recording blackbody radiation at several temperatures. If the optics and walls are maintained at constant temperature for all measurements, the product of I and O and the sum of B and N should be independent of temperature. Instrument response functions theoretically have very slight temperature dependencies. The measurements indicate that the instrument response function varies by less than 3 % over the region 450 to 4000 cm^{-1} (Fig 2.3). The fine structure and limited resolution of the graph in printed form make the differences in the response functions nearly indistinguishable. The fine structure in the figure and the large, negative-going feature at 2600 cm^{-1} are due to gas-phase interference from gases in room air, principally from water and carbon dioxide. The temperature independence of the instrument response function over this temperature range is encouraging.

The sum of detector noise and background radiation is illustrated as a function of wavenumber in Fig. 2.4 and was not allowed to vary with temperature in performing the calculations shown in Fig. 2.3. No optimization of the values was performed. The sum of background and noise values was measured directly by placing a cool, opaque surface over the emission port and assuming all other terms were negligible in Eq. 2.1. The response function was calculated by measuring the response of the system to a blackbody cavity radiator at the several temperatures indicated and solving for the response function in Eq. 2.1, again assuming that all terms other than the background and noise terms were negligible. All spectra were collected at 0.5 cm^{-1} resolution using a 1.5 mm aperture and no apodization or zero filling. Blackbody radiation was generated from a temperature-regulated cavity radiator (Mikron Model 305).

Extraneous radiation from other sources (the term represented by O in Eq. 2.1) is minimized by optical and mechanical means. The aperture diameter at the focal point of the emission beam is sufficiently small (≤ 1.5 mm) to exclude most off-axis contributions to the signal. The optics are contained in a housing with no optical access other than the beam ports. The housing is nitrogen purged, but the effectiveness of the purge is compromised by the access holes. Mirrors and beam splitters are maintained at room temperature and, being on-axis, contribute a small component to the signal since the detector is maintained at cryogenic temperatures (≈ -210 °C). These contributions are included in part in the experimentally determined value of background and noise. The residual contributions from other radiation are ignored in the data analysis.

By far the most difficult portion of the signal with which to deal is the gas-phase interference. Over some regions of the infrared spectrum, the gases are transparent and contribute nothing to the

Figure 2.3 Instrument response functions calculated from blackbody radiation at several temperatures. The fine structure in the response functions represents gas-phase contributions. Theoretically, the response function has virtually no temperature dependence. These measurements, consistent with the theory, indicate little to no temperature dependence.

signal. In regions where the gases are optically active, they emit very strongly and are commonly optically thick. They completely obscure surface emission of the same frequency.

Gas-phase emission peaks cannot be ignored in the data analysis. They have the effect of introducing false features or distorting true features in the resulting spectra [Baxter and Hardesty, 1993 (in press)a]. The approach here is to resolve the spectrum sufficiently that gas-phase peaks can be distinguished from condensed-phase peaks on the basis of their peak widths. The peaks spectrum is then clipped using a Fourier-transform-based algorithm devised specifically for this application [Baxter and Hardesty, 1993 (in press)a].

Verification of data analysis is performed by comparing the measured spectral emissivity from the blackbody source with its known value. This particular radiator has an emissivity of between 0.999 and 1.0. The results are illustrated in Fig. 2.5 for two temperatures not used in calculating the instrument response function. The data illustrated have not been smoothed, and no attempt has been made to eliminate gas-phase interference. The measured blackbody emissivity is seen to vary from 0.98 to 1.02, except where gas-phase emission or absorption peaks give rise to fine

Figure 2.4 Sum of background and noise terms characteristic of the FTIR spectrometer with aperture of 1.5 mm and resolution of 0.5 cm^{-1} in emission mode.

structure. This suggests that emissivities measured by this experimental technique are analytical, i.e., accurate to well within 5 percent.

The fine structure in the results beginning at about 1400 cm^{-1} is due to water. The dominant peak at 670 cm^{-1} is due to carbon dioxide. The fine structure at wavenumbers below 600 cm^{-1} is due in part to interference from atmospheric moisture. It is also an indication of rapidly declining signal-to-noise ratio due predominantly to decaying detector sensitivity. At 450 cm^{-1} and below, the detector has essentially no sensitivity. The results illustrated in Fig. 2.5 cover the region of greatest interest to the spectroscopic study of inorganic species in coal ash deposits.

Approximate and more convenient methods of dealing with Eq. 2.1 have also been developed. These are most useful when either the surface temperature of the deposit is not known or when significant new sources to the term O in Eq. 2.1 have been introduced but not included in the instrument response function. A common example of the latter situation is particle emission and scattering from the particle-laden vitiated flow. Two approximate methods have been used. Both are based on the emission of a clean probe as a reference.

Figure 2.5 Measured spectral emissivities for a blackbody at temperatures higher and lower than those used in determining the instrument response function. The fine structure arises from interference from gas-phase species.

The first method is that of subtraction. The difference between two signals, one from a deposit with unknown spectral variation and one from a reference with known emissivity (ϵ_1) and in the same environment and physical form, is given by

$$\Delta S = S_2 - S_1 = I(\bar{\nu}) \left[\epsilon_{s,2}(\bar{\nu}, T_{s,2}) P_2(\bar{\nu}, T_{s,2}) - \epsilon_{s,1}(\bar{\nu}, T_{s,1}) P_1(\bar{\nu}, T_{s,1}) \right] \quad (2.3)$$

The spectral variation of an unknown sample can be computed if the emissivity of the reference sample, ϵ_1 , is known. The variations in both I and P with wavenumber contain essentially no spectral features. Therefore, all features in the difference can be associated with spectral variations in the deposit emittance. Temperature variations between measurements do not significantly distort the results, but they do change the magnitude of the baseline.

The primary disadvantages of Eq. 2.3 include: (1) relative heights of peaks are distorted because of the nonlinear (albeit smooth) variation in the product of I and P ; (2) baselines take on significant

slopes, potentially confusing locations of maxima in condensed phase features; and (3) the magnitude of the result has little physical significance. Differences in surface temperatures between the two samples change the magnitude of ΔS and introduce some slope in its baseline, but they do not change the location of maxima and minima in the features. Because the wavenumber locations of features and not their magnitude are the most significant data in these results, reasonable ($\pm 40^\circ\text{C}$) temperature variations between the two signals are of little consequence to the result. The primary advantages are: (1) accurate elimination of background contributions (O and B) and (2) ease of analysis.

A second approximate method involves calculating the ratio of the collected spectra and can be used to calculate the emissivity.

$$\epsilon_2(\bar{\nu}, T_2) = \frac{S_2(\bar{\nu}, T_2)}{S_1(\bar{\nu}, T_1)} \epsilon_1(\bar{\nu}, T_1) \quad (2.4)$$

This method assumes that the dominant term in Eq. 2.1 is the emission from the surface (as opposed to emission from the gases or background terms). If the spectral emissivity of the reference surface, ϵ_1 , is known, the spectral emissivity of the sample surface can be calculated. The principal advantages of this method are that physically meaningful results can be obtained and it is relatively easy to implement, both mathematically and optically. Its primary disadvantage is that background and other terms can only be ignored if surface temperatures are high.

Both of the more simplified analyses have been used in the past [Baxter and Hardesty, 1993; Baxter and Hardesty, 1993 (in press)b; Baxter, et al., 1993 (submitted)]. The blackbody source and associated optics were installed and demonstrated this quarter, as discussed above. There have also been improvements in other aspects of the data analysis. Thus far in this fiscal year, spectra have been collected from both metallic and ceramic heat exchange surfaces with surface temperatures varying from 250 to 600 $^\circ\text{C}$. Deposits have been generated from a suite of coals and coal blends ranging in rank from lignite to lv bituminous. Spectra of pure components and mixtures of pure components have been collected and compared with literature data. Much of this work is reported elsewhere [Baxter and Hardesty, 1993; Baxter and Hardesty, 1993 (in press)a; Baxter and Hardesty, 1993 (in press)b].

During the next quarter, data will be analyzed with the blackbody reference technique and some assessments of its quantitative capabilities will be completed. During the last quarter, new spectra from many deposits were collected and previously collected spectra were reexamined to assure that gas-phase emission peaks were not significantly biasing their interpretation. Representative results of these investigations are presented below. Since the data were collected with a variety of different optical configurations, many times with unknown instrument response functions, the simplified analysis procedures are used in their interpretation. In the future, we intend to use the more quantitative procedure.

Results and Interpretation

A typical difference spectrum is illustrated in Fig. 2.6. The emission spectra used to calculate this result were collected from a clean surface and from a coal ash deposit formed from a blend of Eagle Butte and Kentucky #9 coals. Both spectra were collected with a resolution of 2 cm^{-1} , indicating one data point per wavenumber. These spectra result from averaging 256 independently scanned interferograms.

Figure 2.6 Spectral features associated with kaolinite and its product of dehydration, metakaolinite in the range $960\text{--}1140\text{ cm}^{-1}$. The experimental values compare within the precision of the measurement with reference values using a KBr wafer technique.

These spectra were collected from the probe at a surface temperature of about $400\text{ }^{\circ}\text{C}$ ($860\text{ }^{\circ}\text{F}$). Nominal overall particle burnout was over 99 percent. The gas temperature was approximately $900\text{ }^{\circ}\text{C}$ ($1650\text{ }^{\circ}\text{F}$) and oxygen content in the gas was about 3 %. These conditions simulate those found in the latter stages of the convection pass of a utility boiler. More relevantly, these conditions simulate those under which sulfates may form on the surface of heat transfer equipment.

The presence of kaolinite and its decomposition products are indicated in the spectra illustrated in Figure 2.6. The primary spectral peaks for kaolinite occur at about 1100, 1030, 1005, 910 and 540 cm^{-1} , several of which are located in the figure. Secondary peaks occur at 935, 750, 695, and 470 cm^{-1} . The experimental wavenumber values identify the point on the spectrum indicated

by the arrow. Reference values from KBr experiments are also indicated. Reference values for these and other peaks are derived from literature sources [1984; Ferraro, 1982; Nyquist and Kagel, 1971] and from standards prepared in our laboratory on the same probe surfaces under controlled conditions at elevated temperatures. Spectra of some species after exposure to high temperatures are also available [Grim, 1953]. In the interest of objectivity, values from the literature are used for comparison here in making nearly all peak assignments and are designated in the figures as KBr values. Exceptions are limited to those cases where clearly different results were obtained from our references and those in the literature.

Agreement between literature and observed peak locations is complicated by several factors. Literature references are predominately derived from pure, room-temperature samples of micronized mineral pressed in a KBr wafer and examined in transmission using an FTIR or other suitable spectroscopic instrument. By contrast, these *in situ* emission spectra of the ash deposits containing many inorganic phases are collected at combustion temperatures on deposition probes. The sample mixture, morphology, and temperature may alter the spectral signatures. Mixtures of samples may cause weak or broad peaks to become indistinguishable from either the background or peaks from other species. Temperature changes in a material can change the location of a room temperature peak by a few wavenumbers (usually less than 10 cm^{-1}) at $400\text{ }^{\circ}\text{C}$ [Bohren and Huffman, 1983] and as much as 40 cm^{-1} at $1700\text{ }^{\circ}\text{C}$ for halide and oxide crystals [Jasperse, et al., 1966]. The changes can either increase or decrease the wavenumber, although decreases in wavenumber are most common. Changes are also more pronounced for crystalline material than for amorphous material [Mitra and Nudelman, 1970] and are more significant at low wavenumbers than at high wavenumbers. Deposit thickness variations for pure, thin films have been reported in earlier quarterly reports for materials of interest to ash deposition and in the literature for liquids [Hvistendahl, et al., 1983]. Deposit thickness can have a pronounced effect on peak shapes. However, the literature references provide a convenient and available standard with which to compare the measured results.

All of the primary kaolinite peaks except that at 910 cm^{-1} are evident in the spectra, as indicated in the figures. There is a minor peak at 902 cm^{-1} that may be related to the kaolinite peak at 910 cm^{-1} . All other major peaks are located properly within the resolution of the experimental spectrum (2 cm^{-1}) and the reference spectra (typically 4 cm^{-1}).

Recently published, high-temperature, infrared emission spectra collected from a controlled-atmosphere cell illustrate the decomposition of kaolinite to form an intermediate, anhydrous, largely amorphous form (metakaolinite). Under more extreme conditions, mullite and cristobalite are formed [Vassallo, et al., 1992]. The major peak at 910 cm^{-1} and the secondary peaks (at 935 , 750 , 695 , and 470 cm^{-1}) that can not be definitively identified in these *in situ* results are the most strongly affected peaks during the dehydration of kaolinite. The peak at 910 cm^{-1} is associated with the Al-OH stretch in kaolinite and disappears during dehydration. This dehydration occurs between 400 and $600\text{ }^{\circ}\text{C}$, which includes the temperature range of the surface but is below the gas and particle temperature. A reasonable interpretation of these spectra is that the kaolinite underwent dehydration during combustion but did not quantitatively convert to mullite and cristobalite. Upon deposition, it may have partially hydrated, although there is no strong indication of rehydration in these spectra. The reasonably distinct peaks at 1100 , 1032 , and 1002 cm^{-1} indicate that formation of cristobalite and mullite has not proceeded significantly. There is some indication of mullite

formation (minor peak at 550 cm^{-1} , some activity at 1000 and 870 cm^{-1}), but the peaks are not strong and, in the cases of 1000 and 870 cm^{-1} , are assignable to other species.

Figure 2.7 Spectral peaks associated with calcium sulfate in this deposit. The peaks agree most closely with anhydrite and not hydrated forms of calcium sulfate (gypsum). The anhydrite emission peak at 672 cm^{-1} is completely obscured by CO_2 emission from the gas.

An indication of the presence of calcium sulfate, in the form of anhydrite, in the deposit can be derived from the spectra. Figure 2.7 illustrates two of the five major emission peaks for anhydrite. The five peaks are located at 1155 , 1120 , 672 , 615 , and 598 cm^{-1} . The peak at 672 cm^{-1} is completely obscured by CO_2 emission from the gas. However, the remaining peaks are clearly evident and located within the resolution of the spectrum at the reference locations. The features at 1155 and 1120 are located near other spectral features and are illustrated later. Hydrated forms of calcium sulfate exhibit significantly different spectra. Gypsum, for example, has no emission peak at 612 cm^{-1} and little if any discernable difference between the features at 1155 and 1120 cm^{-1} .

Figure 2.8 illustrates the spectral features associated with silica, anhydrite, and other sulfates (glauberite). Micronized, amorphous silica has emission peaks at 465 , 513 , 690 , 775 , 794 , and 1090 cm^{-1} . The peak at 690 cm^{-1} is completely obscured by CO_2 emission, but the other peaks are in regions free from excessive gas-phase interference. The MCT detector has little sensitivity in the

Figure 2.8 Spectral features associated with silica and sulfates in this deposit. The peak at $\approx 1000 \text{ cm}^{-1}$ is nearly coincident with a peak from kaolinite and is difficult to assign unambiguously. The sulfate peaks are not resolved in this spectrum, in contrast with those in Fig. 2.9.

region less than 500 cm^{-1} , and essentially no sensitivity in the region less than 450 cm^{-1} . Therefore, our ability to detect the first two peaks is modest.

Room temperature quartz (α form) has similar peaks ($462, 512, 693, 777, 796$, and 1081 cm^{-1}) to amorphous silica. The α form of quartz undergoes a transition to a β form at about 574°C . During this transition, the peaks in the $770\text{--}800 \text{ cm}^{-1}$ region coalesce to form a singlet at about 792 cm^{-1} . The vibration associated with the peak at 778 cm^{-1} in the α form is forbidden in the β form and the peak at 795 cm^{-1} in the α form shifts to 792 cm^{-1} [Scott and Porto, 1967; Vassallo, et al., 1992]. The feature at $\approx 1100 \text{ cm}^{-1}$ is nearly coincident with a peak from kaolinite and is difficult to assign unambiguously. Taken as a whole, however, the several peaks indicate the presence of some silica, probably in an amorphous form but possibly in combination with α quartz.

Results from the same spectral region but for a Wyodak subbituminous coal are illustrated in Fig. 2.9. There is less indication of anhydrite formation in the Wyodak coal, but significant indication of glauberite. The silica feature at 1089 cm^{-1} is essentially completely obscured by glauberite. The differences in the deposit chemistry between the blend coal and the Wyodak are interesting and will be investigated over the next quarter.

Figure 2.9 Spectral indications of complex sulfates in the Wyodak coal.

Conclusions

Optical design and data analysis for an *in situ*, real-time diagnostic based on emission Fourier transform infrared (FTIR) spectroscopy are presented. The diagnostic has application for measurements in hostile environments. Its utility for monitoring of chemical composition of inorganic species in ash deposits formed during coal combustion is demonstrated.

Deposits are generated in Sandia's Multifuel Combustor, a pilot-scale facility that simulates the temperature and gas composition history experienced by coal particles in commercial-scale boilers. An ash deposition probe is discussed that is designed to simulate conditions at various locations in a boiler while allowing sufficient optical access to make optical measurements. The system is used to analyze the initial layers of ash deposits generated by the combustion of one coal and one coal blend. The Wyodak coal is a subbituminous, western U.S. coal from the Powder River Basin (PRB), and the blend is a mixture of Eagle Butte (also a PRB coal) and Kentucky #9. The latter is a high-volatile bituminous US coal.

The diagnostic can successfully detect the presence of major classes of compounds (oxides, silicates, sulfates) as well as specific species within these classes (silica, kaolinite, anhydrite,

glauberite, etc.). It resolves the time dependence of the formation of ash species on probe surfaces. Its utility for bulk deposit analysis is less certain, since it is primarily sensitive to surface (100 μm to 1 mm) rather than bulk composition. The dependence of the results on composition becomes more complex for thick deposits.

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PLANS FOR NEXT QUARTER

During the next quarter work will focus on finalizing research reports dealing with release mechanisms of inorganic materials from coal and coal and char fragmentation results. These reports will summarize the results obtained in the MFC and will be accompanied by mechanistic interpretations of trends in the data. Also in the next quarter, a summary of progress under this

project to date will be presented at the Ninth Annual Coal Preparation, Utilization, and Environmental Control Contractors Conference, in Pittsburgh, PA, July 19-22, 1993. The paper and presentation materials to be used during this conference have been forwarded to PETC for review. Finally, experiments dealing with two Powder River Basin coals, Black Thunder and Antelope, will be conducted to determine the FTIR diagnostic technique is capable of detecting differences in their behavior. These coals are reported to be nearly identical in their elemental analysis yet commercial experience indicates that their ash behavior is quite different.

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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 Sclippa (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.

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," 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., "Development of Emission FTIR Spectroscopy as a Diagnostic for Ash Deposition During Coal Combustion" to be presented at the Engineering Foundation Conference on Ash Deposition in Boilers, Solihull, UK, June 21-25, 1993.

Baxter L.L., "The Fate of Mineral Matter During Pulverized Coal Combustion," to be presented at the Ninth Annual Coal Preparation, Utilization, and Environmental Control Contractors Conference, Pittsburgh, PA, July 19-22, 1993.

Subtask	FY93											
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
1. Org. & Inorg. Reac.												
a. Experimental												
b. Theoretical												
2. Char Frag. and Fly Ash Formation												
a. Experimental												
b. Theoretical												
3. Spectroscopic Studies												
a. Experimental												
b. Theoretical												

Explanation of Milestones:

- 1.d Completion of research reports on release mechanisms.
- 2.c Complete final report on coal fragmentation.
- 3.e Complete first *in situ* FTIR measurements with coal.
- 3.f Complete first diode laser experiments with coal.
- 3.g Complete first quantitative FTIR experiments with coal ash deposits.
- 3.h Complete first quantitative diode laser experiments with inorganic vapors from coal.

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