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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT

JULY-SEPTEMBER 1993

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

MASTER

COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT — JULY - SEPTEMBER 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 July - September 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, initial forms and distribution of inorganic species in the unreacted coal, and local gas temperature and composition. Also, 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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R.H. Hurt, K.A. Davis, and D.R. Hardesty

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L.L. Baxter and D. R. Hardesty

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT JULY — SEPTEMBER 1993

EXECUTIVE SUMMARY

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

Significant progress was made during this quarter on three subtasks. In Subtask 1.1, reactivity measurements were made on a pyrolysis chars, prepared at Leeds University, derived both from a Pittsburgh #8 whole coal and a vitrinite concentrate. Both samples originate from micronized and density-fractionated coal that has been reagglomerated by a flash pyrolysis technique. Both the flash-pyrolysis char from Pittsburgh #8 whole coal and the vitrinite concentrate burned at a rate closely comparable to the raw Pittsburgh #8 coal, PSOC-1451D in the PETC coal suite. The similarity in burning rates observed for the whole coal and the vitrinite fraction is not surprising, as Pittsburgh #8 is a vitrinite-rich coal.

In Subtask 1.2, a heated-wall reactor was designed and constructed for use in the extended residence time experiments needed for studies of the late stages of combustion and carbon burnout phenomena. The reactor has a cylindrical flow channel defined by a 2" diameter quartz tube surrounded by a vertical, electrically-heated tube furnace with refractory insulation. The quartz reaction tube is placed in a larger alumina tube to shield the burning coal particles from direct radiative exchange with the heating elements. The reactor is designed for sampling studies only, and should provide a useful range of residence times from 20 msec to 500 msec, equivalent to four passes through the existing CCL laminar flow reactor. This development will be discussed in more detail in later quarterly reports.

In Subtask 1.3, the primary development work was completed for a novel captive particle imaging technique. All of the major features of the technique were demonstrated this quarter, the local particle combustion environment was characterized, and the technique was applied for the first time to study char combustion and carbon burnout phenomena. The work in subtask 1.3 on captive particle imaging is described in detail below.

Task 2: The Fate of Mineral Matter

The focus of activity during this quarter was on completing the final reports that summarize the experiments, data, analysis, and conclusions on: (a) the release of iron during coal combustion; (b) the release of inorganic material during coal devolatilization; and (c) fragmentation during coal combustion. The essence of the discussion of the first and last of these is included in this quarterly report. Our work on the second topic has been described in previous quarterly reports.

The investigation of iron release from coal during combustion suggests that chemical reactions of mineral grains should be included as a source of mass in comprehensive descriptions of mineral release from coal or char particles. Iron fume is commonly observed in boiler fly ash at both pilot and commercial scale. The proportion of iron in the submicron particle size is too great to reasonably ascribe its formation to classical vaporization and recondensation processes. This investigation documents the formation of such material and its sensitivity: (a) to the form of iron in coal, (b) oxygen concentration, and coal weathering. Based on extensive experimental data obtained in this work, a mechanism for the loss of iron is postulated that attributes the iron loss to the formation of an iron fume (particles $< 1 \mu\text{m}$) by chemical reaction of porous pyrrhotite grains with oxygen. While preoxidation will most likely decrease the amount of iron fume formation in existing and planned (e.g. Combustion 2000) coal utilization equipment, compared with the pristine, unoxidized samples discussed here, significant iron fume nevertheless will form under many conditions. This significant change in partitioning of iron throughout the fly ash size distribution will affect ash deposition rates, deposit properties, precipitator performance, and most other ash-related issues during pulverized coal combustion.

One of the unique aspects of our work on fragmentation has been the use of the same *in situ* sizing technique to determine both char and fly ash particle sizes. Experiments have been conducted in the Multifuel Combustor (MFC) using utility-grind, pulverized coal in an environment simulating that of a utility-scale boiler. Size distributions have been measured immediately after coal devolatilization and at the end of char combustion (greater than 99% daf burnout as determined from tracer analysis of solid samples). The extent of char fragmentation, as indicated by the number of fly ash particles formed per char particle, is found to depend on char structure, initial char particle size, ash content, and mineral grain size distribution. The data show several significant trends: (1) large char particles produce far more fly ash particles than small char particles; (2) the extent of fragmentation tends to increase with increasing coal rank through hv bituminous; (3) the extent of fragmentation tends to decrease with increasing ash loading; and (4) in all cases studied thus far, the total increase in the number of particles greater than $0.6 \mu\text{m}$ in diameter by char fragmentation is less than a factor of two. Our results indicate substantial agreement among experimental data and conclusions made by other investigators that previously were believed to be in disagreement. In particular, the dependence of char fragmentation on char particle size had not previously been recognized when comparing results from different systems. With regard to practical implications, our data on fragmentation of the parent coal particles (as distinct from the char particles), indicates that no fragmentation occurs during the early stages of coal combustion. Combination of the coal and char data indicate that fragmentation under typical pulverized-coal-fired conditions of particle size and oxygen concentrations: (1) is most significant for cenosphere-forming coals, (2) decreases slightly with increased ash loading, and (3) is a relatively minor effect.

Also this quarter, work continued on the development and application of the FTIR-based surface diagnostic system. This quarter, quantitative (± 0.1) spectral emissivity measurements were obtained, over the range $500 - 3500 \text{ cm}^{-1}$, (2.8 to $20 \mu\text{m}$) for several coals. Results for two Powder River Basin Coals of particular interest to PETC are used to illustrate the results. It is interesting and relevant to note that utility experience with these two coals, in both pulverized-coal and cyclone-fired boilers, suggests that they produce ash deposits having considerably different

properties, despite the similarity in the coal ash analyses. Our results illustrate how the new surface diagnostic can identify these differences *in-situ* and in real time.

Future Work

On the char combustion task, during the next quarter the captive particle imaging experiments on Illinois #6 coal will be continued with the emphasis on dual imaging of visible light and near-infrared particle emission. Captive particle imaging experiments will also be extended to coals of lower and higher rank. In addition, combustion profiles to high conversion will be measured for Illinois #6 and Pittsburgh #8 coals using the new heated-wall reactor in the CCL. These profiles will be used in subsequent quarters to develop and test conversion-dependent kinetic models valid to very high conversion.

Also next quarter, we will apply image analysis techniques to the high-resolution transmission electron micrographs to quantify the degree of molecular ordering observed during combustion of Illinois #6 coal char. These quantitative results will be compared to the results of X-ray diffraction on the same sample set. In addition to improving our understanding of char carbon transformations under combustion conditions, this unique data set will let us evaluate two competing methodologies for tracking the pregraphitization process of coal chars at high temperatures and short times.

On the mineral matter task, during next quarter final reports on iron release during combustion, release of inorganic material during combustion, and coal fragmentation will be completed and submitted to PETC. In addition, further analysis of the FTIR emission spectra obtained in the Multifuel Combustor from ash deposits will continue during the next quarter. Interactions with PETC researchers (Everett Ramer) that were initiated late in this quarter will also continue.

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: July 1 - September 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 are being developed that more accurately describe the char combustion process as it proceeds into the important region of high carbon conversion. One-dimensional combustion models are being 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 are 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 is measured and carbon transformations occurring during the combustion process are 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 is being 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

Significant progress was made this quarter on each of the three active subtasks (the project plan does not specify work on subtask 1.4 during this quarter). In Subtask 1.1, reactivity measurements were made on a pyrolysis chars, prepared at Leeds University, derived both from a Pittsburgh #8 whole coal and a vitrinite concentrate. Both samples originate from micronized and density-fractionated coal that has been reagglomerated by a flash pyrolysis technique. Both the flash-pyrolysis char from Pittsburgh #8 whole coal and the vitrinite concentrate burned at a rate closely comparable to the raw Pittsburgh #8 coal, PSOC-1451D in the PETC coal suite. The similarity in burning rates observed for the whole coal and the vitrinite fraction is not surprising, as Pittsburgh #8 is a vitrinite-rich coal.

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In Subtask 1.3, the primary development work was completed for a novel captive particle imaging technique. All of the major features of the technique were demonstrated this quarter, the local particle combustion environment was characterized, and the technique was applied for the first time to study char combustion and carbon burnout phenomena. The work in subtask 1.3 on captive particle imaging is described in detail below.

Investigation of Char Combustion and Burnout through Captive Particle Imaging (CPI)

This section describes the development of a novel imaging technique in the CCL and its initial application to the study of char combustion and carbon burnout phenomena.

Background and motivation

To date, the char combustion effort at Sandia has used *in situ* optical measurements on particles in entrained flows as the primary tool for studying coal char combustion. Indeed, these *in situ* measurements of the sizes, temperatures, velocities, and emissive factors of individual burning char particles has provided a detailed quantitative description of the process. This data comes, however, in the form of particle population statistics at various residence times and cannot be used directly to describe how the combustion behavior of any given particle or class of particles evolves in time. Complementary information can be obtained by a technique that tracks single particles throughout their complete combustion lifetimes. Such a technique would be especially useful for

investigating the latter stages of combustion and carbon burnout phenomena, topics that are the focus of the present phase of the project.

Previous studies

A number of previous studies of pulverized coal combustion have used single-particle imaging techniques in one form or another, starting with the early studies of Godbert (1930) and Orning (1942). McLean, et al. (1981) obtained images of entrained coal particles and their associated soot clouds during devolatilization using high-speed photography. Similar images have been obtained by holographic techniques (Seeker et al., 1981). Schroeder et al., (1992) have devised a technique for automated acquisition of still images of entrained coal particles during both devolatilization and combustion using a CCD array detector and laser trigger. These images were used to distinguish soot agglomerates from char particles found early in the combustion process. Each of these studies focused on acquisition of single images, or image sequences of only a portion of the combustion process, rather than image sequences of entire particle combustion histories. In addition, the optical systems do not have sufficient resolution or light-gathering power to image details of particle surface morphology.

Timothy, et al. (1986) have used high-speed cinematography to study the formation and burnout of soot clouds surrounding entrained pulverized coal particles in the early phases of combustion. In order to capture a large portion of the combustion lifetime of individual particles in the field-of-view, relatively low magnifications were employed which do not yield detailed information about particle structure or behavior. Thomas and coworkers at the CSIRO have developed a captive particle imaging technique for the study of coal devolatilization and combustion (Thomas et al., 1992, 1993). The technique uses laser radiation to heat, at a controlled rate, particles that are affixed to the tip of a fine needle. This approach allows particles of chosen petrology to be hand-selected and mounted for imaging, a feature which has proven useful for distinguishing between reactive (fusible) and nonfusible inertinite under realistic heating rates and temperatures. The work of this group has led to a very useful captive particle imaging technique, but one that is designed to address very different issues than those of interest to the present project.

In addition to these studies, electrodynamic balances have been employed to suspend single coal/char particles, whose combustion behavior can then be studied in the absence of possible interferences by mechanical suspension devices. The operation of these devices is, however, currently limited to low particle temperatures; at the high temperatures relevant to entrained flow combustion, electric charge loss by thermionic emission or other mechanisms prevents continuous electrodynamic suspension. Electrodynamic balances have thus not yet been used in high temperature studies of carbon burnout.

For this project, a single particle imaging technique was developed that provides:

1. an accurate simulation of the gas-particle transport processes in entrained-flow combustion
2. detailed information on single particle behavior and morphology for particles of 200 μm and less. This requires an imaging resolution of 2 - 5 μm , which puts significant

constraints on the optical design. Because the optical properties of elemental carbon and fly ash differ greatly, such images provide a wealth of information on ash/carbon interactions, the timing of the visible carbon-to-ash transition at high burnout. Of particular interest is the particle morphology and carbon content at the point of near-extinction in the latter phases of burnout.

3. quantitative measurement of radiant emission from the particle. The spectral radiance is a measure of the combustion reaction intensity and can be used to infer quantitative reaction rates in environments where mass and energy transport are well characterized. Techniques using laser heating are unsuitable, as the particle temperatures are greatly affected by the laser absorption processes within the particle, which are complex and difficult to model.

The technique described below embodies these above three features and provides unique information on extinction and final burnout, ash/carbon interactions, the reactivity and burnout of various particle morphological types, and fragmentation.

The principle of captive particle imaging

It is not practical to image particle trajectories in the entrained phase at extremely high resolutions (2 - 5 μm) due to uncertainty in the particle location coupled to inherent limitations on optical depth-of-field. Indeed, high resolution imaging requires that particle positions be known at all times with an accuracy equivalent to the depth-of-field of the imaging system, which is typically on the order of a single particle diameter. The particle position can be fixed through use of a mechanical suspension device *if* the device does not interfere with the gas-particle mass and energy transport processes.

A mechanical suspension technique for char combustion studies was designed, recognizing that gas-particle transport, for particles in the pulverized size range under most conditions, is dominated by diffusion, conduction, and radiation, and not by convection. (Note that convection does play a role in the combustion of larger particles, and in other combustion subprocesses such as devolatilization.) For char combustion, however, the suspension device can be allowed to perturb the flow field and the convective processes, if it does not present a significant barrier to diffusion, conduction, or radiation to and from the particle. A properly designed porous particle support having a very low solid volume fraction, V_s , (on the order of one volume % or less) was chosen to meet these requirements. The support is made of fibers that are much finer than the particles of interest, to ensure that the solid volume fraction of the support in the immediate vicinity of the particle is small. (A coarse grid may have a low solid volume fraction on the average, but may have the effect of a solid substrate in the local environment of a fine particle in direct contact with one of the solid grid elements.) The layer of fine fibers perturbs the flow field substantially due to its high surface area, but does not perturb conduction or diffusion processes due to its low solid volume fraction.

In addition to the design of a nonintrusive particle support, many other issues were considered in the development of the captive particle imaging apparatus. These issues include optical design, design of a flow configuration that prevents particle entrainment, and development of technique for

initiating combustion in a brief and well-defined transition period. The complete apparatus is described in some detail in the following section.

Apparatus and experimental procedures

Figure 1 depicts the captive particle imaging apparatus. The experimental procedure is first described in general terms, followed by more detailed discussions of the individual components.

Experimental procedure. Char particles of 100 - 200 μm in diameter, previously prepared by raw coal injection into the CCL laminar flow reactor, are placed on a low-density particle support and reinserted into the flow reactor through a open test section in the quartz reactor wall (see Fig. 1). The support is surrounded by a small conical cooling coil which maintains the particle at 200 - 300 $^{\circ}\text{C}$, while it is brought into the focal volume of a modified long-focal-length microscope. The cooling coil is then retracted, the particle is rapidly heated by the surrounding gases, and its ignition, combustion, and burnout behavior is imaged at high resolution using both reflected visible light and emitted light in the near infrared.

Particle support. The particle support consists of a platinum ring, spanned in several places by 75 μm diameter platinum thermocouple wires that provide support for a thin layer of fine (5 μm diameter) Al_2O_3 fibers. The Al_2O_3 (99% pure) is deposited by placing a drop of a dilute aqueous fiber suspension on the platinum grid and evaporating the water by insertion in the post-flame gases. Each particle contacts the inert alumina fiber substrate at only a few points. The low solid volume fraction of the fiber bed provides an environment in which diffusion, conduction, and radiation occur much as they do for entrained particles.

Quantitative estimates can be made of the extent to which the particle support perturbs diffusion, conduction, and radiative transfer to and from the particle. The effective diffusion coefficient, D_{eff} , in a porous medium is commonly expressed as

$$D_{\text{eff}} = D \Theta / \tau \quad (1.1)$$

where D is the molecular diffusion coefficient, Θ is the porosity ($1 - V_s$), and τ is an empirical tortuosity coefficient (Satterfield, 1981). As solid volume fraction approaches zero, the porosity and tortuosity approach one, and the effective diffusion coefficient approaches the molecular diffusion coefficient. Pressed sheets of the alumina fibers have reported solid volume fractions of 4%; the alumina gossamers formed by the gentle deposition technique used here are likely to have solid volume fractions somewhat lower. The effective diffusion coefficient through this bed, D_{eff} , is therefore predicted by Eq. 1 to be greater than 96% of the molecular diffusion coefficient, D . The fiber bed thus provides no significant barrier to diffusion.

Conduction and radiation processes are expected to be very similar to those occurring in the free stream for very light fiber loadings. For the heavier fiber loadings used in some experiments however, the effect is not as clear. Assuming a worst case in which the bed is thick and has a solid volume fraction equal to the pressed insulating paper product (4%), the maximum perturbation to the heat transfer processes can be estimated. The thick fiber bed will radiate heat to the particle according to:

Figure 1. Schematic of the flow reactor and optical systems in the captive particle imaging experiment.

$$q_r = F \epsilon \sigma T^4 \quad (1.2)$$

where q_r is the radiative flux from the support to the particle at the particle surface, F is the hemispherical view factor (1/2), ϵ is the total emissivity of alumina at 1300 K (≈ 0.4), σ is the Stefan-Boltzmann constant, and T is the support temperature. For equal particle and support temperatures the radiative flux from the support to the particle, expressed as a fraction of the total radiative flux from the particle to its surroundings, is:

$$q_r / q_p = (F / 1) (\epsilon / \epsilon_p) = (0.5)(0.5) = 0.25 \quad (1.3)$$

where ϵ_p is the particle total emissivity (≈ 0.8). The maximum radiative contribution of the fiber bed is therefore one-fourth of the radiative heat loss from the particle, and will be less during rapid combustion, when the particle temperature is significantly hotter than its surroundings. With respect to radiation, therefore, the local particle environment in the CPI experiments approximates the environment experienced by particle entrained in optically thin gas streams surrounded by cool walls (as in the CCL experiments).

Based on reported thermal conductivities of the pressed alumina paper, the effective thermal conductivity of the particle environment can be increased by as much as 50% by the presence of a particle support with heavy fiber loading. The modest enhancement of conductive transfer rates from the particle will not change the basic features of single particle combustion, but may reduce somewhat the absolute values of particle temperature during the rapid combustion stage. Before quantitative combustion rates can be computed from measured particle temperatures (a longer term goal), more work is needed to determine the critical fiber loadings that ensure that the free-stream heat transfer processes are not perturbed.

Cooling coil. Of several techniques explored, the conical cooling coil (see Fig. 1) provides the best protection for the particles prior to the beginning of the experiment and the most rapid and characterizable transition to combustion conditions. Quartz sheaths, with and without inert purge gas flows, were also evaluated over the course of this development, but were found inferior for a number of reasons. For example, the presence of quartz surface was found to shift the focal point of the microscope to such an extent that very poor images were obtained after removal of the sheath.

The most advantageous feature of the cooling coil is that it avoids local concentration transients at the beginning of the experiment, which would be difficult to characterize. Using the cooling coil, the gas composition is established prior to the start of the experiment, and the combustion is initiated solely by a rapid increase in local temperature. The temperature transients can be thoroughly characterized by fine-wire thermocouples with bead sizes comparable to the particle sizes of interest. The thermocouple measurements, which are described in a later section, completely define the local particle environment, including the initial transient period.

Modified long-focal-length microscope. The high resolution required (2 - 5 μm), combined with the need to isolate the collection optics from the high-temperature combustion environment, necessitate large diameter microscope optics. Recent advances in long-focal-length microscopes make 2 - 5 μm resolution possible at working distances of 3 - 6 inches in a flexible refracting

system with exchangeable objectives. The microscope used is the model K2 of Infinity Photo-Optical, modified with a Nikon photoquadrocular head, providing beam splitters for three simultaneous viewing/photography ports. A binocular eyepiece port is used for convenient view finding, and two other ports are equipped with optical filters and remote-head CCD video cameras (see Fig. 1).

The two photography ports are used to obtain dual video image sequences of the same field-of-view. A color CCD camera is attached to the first photography port to image visible light, which is introduced through a fiber-optic and reflected off the particle and support surfaces. At high particle temperatures, solid phase incandescence can also be observed as a red glow emitted by the particles. These images are useful for tracking particle morphological changes and for tracking the process of carbon burnout, which changes the optical properties of the particle from those characteristic of elemental carbon (highly absorbing) to those characteristic of ash (generally reflective). The second independent imaging system records the near-infrared particle incandescence. An optical band in the near infrared from 700 - 1000 μm is selectively imaged by incorporating a Schott colored-glass filter in the quadrocular head, and reflected radiation in the same wavelength band is rejected by placement of an infrared filter in the fiber optic illuminator. The fiber-optic illumination is rejected so successfully, that this second optical channel records no image whatsoever until the particles reach high temperature and begin to emit significantly in the near-infrared. The incandescent images provide information on the particle temperature and the intensity of the combustion reaction, and are useful for studying char reactivity and extinction phenomena.

Image acquisition systems. The dual video image sequences are independently acquired, displayed, and stored. The color visible images from the first channel are displayed and recorded on Super-VHS tape. The near-infrared images are acquired by a digital system for quantitative analysis off-line. The digital system uses the Data Translation DT3851 frame grabber on an IBM-compatible 486 platform and Global Lab Image acquisition and processing software. The DT3851 frame grabber has the unique capability of recording image sequences at or near video rates (30 Hz) by incorporating up to eight megabytes of buffer memory on board. Image transfer to the host computer memory is too slow to keep pace with video framing rates. Image files are stored on SyquestTM removable hard drives and are processed by several software packages, including *Global Lab Image*TM, *Color-It*TM, and *Neopaint*TM.

Combustion lifetimes of particles are typically from 1 to 3 seconds under these conditions, with a final ash-decarburization phase that can persist for 20 seconds or longer. The entire process requires acquisition of approximately 10000 video fields acquired at a rate of 60 fields/sec, and is easily stored on tape for qualitative analyses. The digital image acquisition system used for quantitative analysis of near-infrared incandescence is limited to a total of approximately 30 total frames when sampling at or near video rates of 60 fields/sec. The digital image sequences are therefore acquired at one-half to one-third of standard video rates, and the image sequences are stored in on-board buffers. This results in approximately 8 megabytes of image data for each particle, and covers most of the 1 - 3 seconds of the primary combustion process. Incandescent

images are not obtained during the final ash-decarburization phase. This does not represent a significant loss of information, because the significant changes in particle temperature and radiance that correspond to ignition, rapid combustion, and near-extinction, occur earlier in the process.

The two video channels yield independent asynchronous image sequences for which a common time reference is needed. This is currently established using a collimated light source that is redirected by 90 degrees toward the microscope by a mirror mounted on the cooling coil shaft. As the shaft and cooling coil are retracted, a short pulse of light falls on the microscope objective when the mirror crosses the collimated beam. This light flash is recorded by both imaging systems and can be recognized during frame-by-frame examination after the experiment and used as a time reference to put both image sequences on a common time basis.

Characterization of flow field, temperatures and temperature transients

Figure 2 shows a photograph of the flow streamlines in the vicinity of the particle support, imaged by seeding the flow on the centerline with 5 μm alumina particles. The support is seen to perturb the flow significantly, producing curved streamlines on the approach side and distinct recirculation zones in the downstream wake. The high surface area alumina fiber bed is a significant obstacle to the flow and redirects much of the approaching fluid around the edge of the support. The local velocity in the immediate vicinity of the top of the alumina fiber bed is believed to be much lower than the free stream velocity. This is consistent with the observation that many particles in the 100 - 200 μm size range remain on the top side of the support when the cooling coil is removed. Some particles are lost, however, by entrainment into the bulk flow, but sufficient fraction of the particles remains to make the technique useful.

The fact that some particles are entrained and others are not suggests that the local velocities are on the order of the terminal velocity for particles of this size and density, about 5 cm/sec. As the relative gas-particle velocities increase from 0 and 50 cm/sec, the Nusselt and Scherwood numbers (describing heat and mass transfer respectively) increase from a value of 2 to approximately 2.3. Thus for relative gas-particle velocities less than 50 cm/sec, the technique provides a good simulation of the mass and energy transport processes for particles in the free stream. Higher relative gas-particle velocities could, in principle, lead to enhanced mass and energy transport, but, in practice, these velocities cause particle entrainment and make imaging impossible.

Table 1 presents steady-state radiation-corrected temperatures measured by fine-wire thermocouples, whose beads were placed on the alumina fiber bed in the same manner as the char particles during combustion experiments. Temperatures at various locations on the alumina fiber bed are uniform within 20 $^{\circ}\text{C}$. Steady-state temperatures are observed to be a function of the alumina fiber loading, increasing by about 20 $^{\circ}\text{C}$ as the alumina loading is increased from light to heavy. During combustion experiments we strive for reproducible light-to-moderate loadings, and estimate that normal variations in alumina loading give rise to differences in steady-state temperatures of approximately 10 $^{\circ}\text{C}$. Temperatures inside the cooling coil vary from 240 to 285 $^{\circ}\text{C}$ with a mean value of 260 $^{\circ}\text{C}$.

Figure 2. Streamlines in the local flow field surrounding the CPI particle support. Flow is seeded on the centerline with 5 μm alumina powder. Image formation here is primarily due to particle scattering of fiber-optic-supplied white-light illumination.

Table 1.
Local gas temperatures in the particle environment during
captive particle imaging experiments

<i>Distance from burner face (cm)</i>	<i>Temperature inside coil (K)</i>	<i>Steady-state temperature after coil retraction (K)</i>
6.4	530	1360
12.7	530	1325
25.4	530	1250

Figures 3 - 5 present time-resolved temperature measurements taken at 1000 Hz during removal of the cooling coil under various conditions. The data were taken with an IBM 486 computer equipped with an A/D board specially designed for thermocouple (low voltage) input. Maximum heating rates were observed to be approximately $2 \cdot 10^3$ K/sec. Figure 3 demonstrates good shot-to-shot reproducibility of the temperature transient. Figure 4 shows the transients for various oxygen levels and and Fig. 5 demonstrates the effect of alumina fiber loading. Increasing alumina loading increases the time required to reach 90% of the final temperature rise from approximately 100 to 400 msec.

In summary, the rapid and reproducible temperature transients combined with the avoidance of transients in gas composition make this flow configuration very useful for investigating char combustion and burnout phenomena. The finite heating rate does limit useful experiments to those conditions (temperatures, oxygen levels, and particle sizes) that result in total burnout times of about 500 msec or greater. These conditions overlap significantly with the parameter space of interest in pulverized coal combustion, so that the finite heating rate is not a serious limitation for the application of the technique to the present project. The technique is also capable of revealing the qualitative features of more rapid combustion events, but, in these cases, much of the reaction occurs in a zone in which the gas temperature is changing rapidly, making quantitative analyses difficult.

Figure 3. Temperature transients during captive particle imaging. Comparison of three trials under identical conditions demonstrates good shot-to-shot reproducibility.

Figure 4. Temperature transients during captive particle imaging in gas environments with varying oxygen levels.

Figure 5. Effect of fiber loading on final temperature and temperature transient for two gas environments. The effect of light fiber loading was examined in 3% oxygen at a free-stream gas temperature of 1350 K. The effect of heavy fiber loading was examined in 6% oxygen at a free-stream gas temperature of 1280 K.

Application to coal char combustion and carbon burnout

Illinois #6 coal was chosen to be the subject of the initial study, as the information obtained leverages the extensive characterization of chars from this coal presented in the previous two quarterly reports. The char was prepared from 125 - 210 μm Illinois #6 coal particles by injection into the 6% oxygen environment of the CCL laminar flow reactor and rapidly quenched and extracted at 47 msec time, at the approximate end of devolatilization and beginning of char combustion. A small number of these char particles were then loaded onto the particle support, the support was placed inside the cooling coil in the high temperature vitiated air stream, and the imaging system was focused on a single selected particle from the group. At this point the image acquisition systems were activated, the coil retracted and char combustion initiated. Image sequences were obtained in this way for approximately 50 Illinois #6 char particles under various conditions, using both single and dual camera configurations.

Figures 6 - 8 present excerpts from selected image sequences, illustrating the typical behaviors observed. The particles in both Figs. 6 and 7 (nominal initial diameter 150 μm) clearly illustrate the multistage nature of the char burnout process, previously inferred from *in situ* optical measurements in the CCL (Hurt et al., 1993a,b). Shortly after retraction of the cooling coil, a bright red incandescence appears in the single camera experiments for each of the particles burning in 6 mole-% oxygen. The red emission clearly originates from the particle surfaces and not from aerosol or gas-phase species in the boundary layer, as the emission closely follows the particle periphery and surface topology, even at very high resolution. The solid-phase emission indicates an elevated particle temperature, which is a consequence of heat transfer from the surrounding gas as well as the exothermic heterogeneous combustion reactions.

The bright incandescence in Figs. 6 and 7 lasts for a period of about 0.5 seconds before fading, indicating a period of early rapid combustion, followed by a loss of global reactivity and a decrease in particle temperature. This has been referred to as a near-extinction event (Hurt, 1993) and occurs when the global particle combustion rate has decreased to such an extent that the rate of heat release is no longer sufficient to maintain the temperature of the particle substantially above the temperature of the local environment. The existence of near-extinction events and the two stage nature of the char combustion process has previously been inferred from *in situ* optical measurements in the CCL, and is discussed in detail elsewhere (Hurt, 1993, Hurt and Hardesty, 1992a).

The third frame in each image sequence shows the particle morphology immediately after the end of the rapid combustion phase. The particle in Fig. 6 is still optically black at this point, with ash just becoming visible at the particle surface and edges. The particle in Fig. 7 exhibits somewhat more surface ash, but still contains a significant amount of elemental carbon visible on the particle exterior. The dual camera experiments, which are better suited for quantitative tracking of particle incandescence, indicate that particle temperatures begin to decrease *before* there are noticeable changes in the appearance or optical properties of the particles. After the near extinction event, the global combustion rate slows dramatically, converting the carbon-rich particles to inorganic-rich particles, which contain elemental carbon in their cores or as islands within a coherent inorganic matrix. The final stage of the combustion process consists of the removal of these elemental carbon inclusions from the predominately inorganic matrices. This process, which we have

Figure 6. Typical time-indexed captive particle image sequence for combustion of Illinois #6 coal char. Combustion is in 6 mole-% oxygen at a steady-state gas temperature of 1360 K. Nominal initial particle diameter is 150 μm .

Figure 7. Typical time-indexed captive particle image sequence for combustion of Illinois #6 coal char. Combustion is in 6 mole-% oxygen at a steady-state gas temperature of 1360 K. Nominal initial particle diameter is 150 μm .

referred to as "ash decarburization" is extremely slow, requiring 10 - 30 seconds for the particles represented in Figs. 6 and 7.

The detailed information present in image sequences such as Figs. 6 and 7, justifies an extension of the conceptual subdivision of the carbon burnout process from the two-stages initially proposed (Hurt, 1993) to three, as suggested by earlier results from off-line analyses (Hurt et al., 1993). Each of the following three stages have been directly observed in captive particle imaging experiments: (1) early char combustion, which proceeds rapidly and at high temperature; (2) late char combustion which converts carbon-rich particles to mixed particle types at lower temperatures and reduced rates; and (3) decarburization of ash. The carbon burnout process is clearly seen to be asymptotic in nature, in contrast to the predictions of global kinetic models (Hurt, 1993).

Several other general observations can be made from the captive particle experiments on Illinois #6 coal char. First, the particle incandescence is brighter and the burnout times shorter in 6% oxygen than in 3%. The maximum brightness, which is a function of the maximum particle temperature, is seen to vary significantly from particle to particle under identical conditions. Both of these observations are consistent with the general features of char combustion, as revealed by *in-situ* optical data optical in the CCL.

Also, certain qualitative differences are observed in the combustion behavior from particle-to-particle, which are related to differences in initial inorganic content and particle density. Dense particles, with a high initial inorganic content, react to leave large, cohesive ash particle frameworks that are similar to the parent particle in shape. The primary visible feature of the combustion process for these particles is the change in color from black to near-white as elemental carbon is consumed. No dissociation, fragmentation, or rearrangement of the particles is observed. The ash frameworks are often observed, however, to slowly consolidate and densify after most of the carbon disappears, due either to sintering mechanisms, or to simple rearrangement of the fine mineral grains comprising the agglomerate.

Low-density, low inorganic-content particles behave in a very different way, undergoing profound morphological changes during combustion, as seen by the example in Fig. 8. The particle in Fig. 8 is typical of many char particles from swelling coals; it has a vesicular structure, including one or several large central cavities, with much of the carbon concentrated in a membrane-like shell on the particle periphery. For particles of this type, the initial CPI experiments show that combustion first destroys the coherent outer shell, leaving a fragile framework that then fractures and collapses, ultimately leading to an ash particle that is very much smaller than the original char particle. Figure 8c shows an example of such a fragile framework formed during the intermediate stages of combustion from a char particle of low-density and low ash content. These low-density particles are thus much more likely to dissociate during combustion, in agreement with the conclusions of Baxter (1992).

Instead of ultimately producing distinct fragments, however, the dissociated products are typically observed to reagglomerate to yield a single ash particle. Perimeter fracture was also observed in one case during the initial CPI experiments, but here as well, the products were not released as fragments, but were observed to reattach to the primary particle, which eventually collapsed to a single particle of ash.

Figure 8. Selected captive-particle images illustrating the combustion behavior of a low-density, low-ash content particle of Illinois #6 char. Combustion in 6 mole-% oxygen at a local gas temperature of 1360 K.

In general, the fate of the fragments formed by morphological dissociation of a highly reacted char particle is expected to depend on a balance of attractive forces between the fine fragments and inertial or aerodynamic forces that tend to disrupt the fragile agglomerate. Under the conditions prevailing in the captive particle imaging experiment, fragmentation is observed to be an exceptional or rare, rather than typical behavior. This result implies that fragmentation models need to be modified to account for the binding tendency of surface forces between distinct particle fragments or mineral grains in the colloidal size range.

Conclusions

1. During this quarter, development of a new captive particle imaging system was completed. The system was applied to obtain qualitative data on char combustion and carbon burnout phenomena for Illinois #6 char particles. Both single camera experiments and dual camera experiments, with separate imaging of visible light and near-infrared particle incandescence, provide insights into the process of char combustion to complete carbon burnout.

2. The basic features of char combustion to complete burnout that were previously inferred from *in situ* optical data have now been confirmed by direct observation. Single particle combustion comprises three stages more or less distinct stages: (1) early char combustion, which proceeds rapidly and at high temperature; (2) late char combustion, which begins after a near-extinction event, and converts carbon-rich particles to mixed particle types at a lower temperature and a slower rates; and (3) decarburization of ash. The initial image sequences provide dramatic illustration of the asymptotic nature of the char burnout process and provide, for the first time, a measure of the extremely long time scales required to remove residual carbon inclusions from inorganic (ash) frameworks in the very late stages of pulverized coal combustion. This work confirms the need for improved char combustion models that account for the asymptotic nature of the process.

3. For dense, high-ash-content particles, the inorganic matter is typically observed to form a cohesive framework, which is similar to the parent particle in shape, and which prevents particle fragmentation or rearrangement even as complete carbon burnout is approached. In contrast, low-density, low-ash-content char particles undergo profound morphological changes during combustion. These particles are much more likely to dissociate during combustion, but instead of releasing distinct fragments, the fractured particles typically reaggregate and collapse to yield a single fine ash particle under the experimental conditions investigated to date.

4. The extent of char particle fragmentation is most likely influenced by surface forces acting between distinct carbon fragments. The fate of the fragments formed by morphological dissociation of a highly reacted char particle is expected to depend on a balance of attractive forces between the fine fragments and inertial or aerodynamic forces that may disrupt the fragile agglomerate. This result implies that fragmentation models need to be modified to account for the binding tendency of surface forces between distinct particle fragments or mineral grains in the colloidal size range.

FUTURE PLANS

During the next quarter, the captive particle imaging experiments on Illinois #6 coal will be continued with the emphasis on dual imaging of visible light and near-infrared particle emission. Captive particle imaging experiments will also be extended to coals of lower and higher rank. In addition, combustion profiles to high conversion will be measured for Illinois #6 and Pittsburgh #8 coals using the new heated-wall reactor in the CCL. These profiles will be used in subsequent quarters to develop and test conversion-dependent kinetic models valid to very high conversion.

Also next quarter, we will apply image analysis techniques to the high-resolution transmission electron micrographs to quantify the degree of molecular ordering observed during combustion of Illinois #6 coal char. These quantitative results will be compared to the results of X-ray diffraction on the same sample set. In addition to improving our understanding of char carbon transformations under combustion conditions, this unique data set will let us evaluate two competing methodologies for tracking the pregraphitization process of coal chars at high temperatures and short times.

NOMENCLATURE FOR TASK 1

F	hemispherical view factor
q	combustion rate, g-carbon/s-cm ²
q_r	radiative heat flux to the particle from the particle support, W/m ² -s
q_p	radiative heat flux from the particle to its entire surroundings, W/m ² -s
T	temperature of the particle support, K
T_g	gas temperature, K
T_p	particle temperature, K

Greek symbols

ϵ	total emissivity of alumina at 1300 K (≈ 0.4)
ϵ_p	total emissivity of the char particle (≈ 0.8)
ρ_c	carbon density, g-carbon/cm ³ -particle
σ	Stefan-Boltzmann constant
τ	residence time, msec

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ACKNOWLEDGMENTS

The technical contributions of James Ross, Richard Yee, Scott Kelly, and Carlos Gethers are gratefully acknowledged.

PUBLICATIONS, PAPERS, AND PRESENTATIONS

This quarter, a paper was presented at the *PETC Ninth Annual Coal Preparation, Utilization, and Environmental Control Contractor's Conference* in Pittsburgh. A second paper on research sponsored by both EPRI and PETC was presented at the *7th International Conference on Coal Science* in Banff, Alberta in September. Kevin Davis also presented a paper at the *1993 Pittsburgh Coal Conference* on PETC-sponsored research.

Two papers on PETC-sponsored research received final acceptance for archival publication this quarter. An article entitled: "Reactivity Distributions and Extinction Phenomena in Coal Char Combustion" by R. H. Hurt will appear in *Energy and Fuels*, and a brief correspondence entitled "Gasification-Induced Densification of Carbons: From Soot to Form Coke" by R. H. Hurt, A. F. Sarofim, and J. P. Longwell will appear in *Combustion and Flame*. This latter note does not contain experimental results from the CCL, but offers a reinterpretation of recent literature data and reviews the rapidly expanding literature on carbon densification.

COLLABORATIONS, VISITORS, CONTRIBUTING PERSONNEL

Richard Yee returned from the University of California, Davis, for his second summer working in the CCL. Richard's efforts focused on the final development and application of the captive particle imaging technique. Collaborations continued with Professor Jon Gibbins at Imperial College, and with Sandians Nancy Yang (California) and Thomas Headley (New Mexico).

Task 1 Milestone Chart

Subtask	FY93		FY94											
	A	S	O	N	D	J	F	M	A	M	J	J	A	S
1. Kinetics of heterogeneous particle populations	1a ▼												1b ▽	
2. High carbon conversion			2a ▽				2b ▽						2c ▽	
3. Captive particle imaging	3a ▼			3b ▽			3c ▽	3d ▽						
4. Data unification										4a ▽		4b ▽		4c ▽

Milestones

1a. reactivity measurements completed on Pittsburgh #8 whole coal and vitrinite concentrates

1b. characterization completed of variations in ash content, carbon density, and reactivity, and the cross correlation terms for Illinois #6. (The combination of these variabilities determines variability in burnout times.)

2a. quantitative analysis complete of the degree of carbon molecular ordering during combustion for Illinois #6 char

2b. burnout profiles measured in the long residence-time reactor for 3 - 4 coals

2c. reactivities of the heat-treated samples measured in the CCL

3a. development of the captive particle imaging apparatus complete

3b. quantitative calibration complete of particle radiance measurement capability for the captive particle imaging experiment

3c. captive particle experiments complete on 4 coals

3d. image analysis complete

4a. experimental work complete

4b. conversion dependent model formulated, accounting for heterogeneity and conversion-dependent reactivities

4c. model tested and fitted to the burnout profiles for 3 - 4 coals

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: July 1, 1993 - September 30, 1993

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

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

OBJECTIVES FOR TASK 2

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

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

**SUBTASK 2.1 TRANSFORMATIONS: RELEASE OF INORGANIC MATERIAL DURING
COAL COMBUSTION**

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

The goal of this subtask is to test the hypothesis that some inorganic species are released from coal particles during coal devolatilization and char oxidation. Particular focus is on mechanisms of release other than ash vaporization. Material release effected by coal devolatilization involves the

small-grained and organically-associated minerals, many of which are strongly implicated in deposit formation in commercial-scale boilers. Mineral release associated with inorganic reactivity includes thermally unstable or chemically reactive material such as pyrite and calcite, both of which play significant roles in deposit formation and properties. This subtask uses data collected in each of the three coal reactors at Sandia and tests several ranks of coal at several rates of devolatilization.

SUBTASK 2.2 THE EVOLUTION OF PARTICLE AND FLY ASH SIZE DISTRIBUTIONS

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

SUBTASK 2.3 SPECTROSCOPIC STUDIES OF INORGANIC PHASES

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

SUMMARY OF TECHNICAL PROGRESS DURING THIS QUARTER

Topical reports on the release of iron during coal combustion, the release of inorganic material generally during coal devolatilization, and coal fragmentation are nearing completion. Work during this quarter focused primarily on finishing these reports. The reports will be submitted to PETC under separate cover. Under Subtasks 2.1 and 2.2 of this quarterly report, we summarize the principal discussion found in these reports. Most of the coal characterization and data to be in the appendixes of the topical reports are not included in this quarterly report. Also, the discussion of inorganic release during coal devolatilization is not summarized here. The discussion in Subtask 2.3 highlights the computation of spectral emissivities from coals and how they change during ash deposit growth.

SUBTASK 2.1 TRANSFORMATIONS: RELEASE OF INORGANIC MATERIAL DURING COAL COMBUSTION

Abstract

A series of investigations of iron release during combustion is reported for a suite of coals ranging in rank from lignite to low-volatile (lv) bituminous coal under combustion conditions ranging from oxidizing to inert. Experimental measurements are described in which, under selected conditions, major fractions of the iron in the coal are released within a 25 ms period immediately following

coal devolatilization. Mechanistic interpretation of the data suggest that the iron is released as a consequence of oxygen attack on porous pyrrhotite particles. Experimental testing of the proposed mechanism reveals that the release is dependent on the presence of both pyrite in the raw coal and oxygen in the gas phase, that slow preoxidation (weathering) of the pyrite significantly inhibits the iron release, and that iron loss increases as oxygen penetration of the particle increases. Each observation is consistent with the postulated mechanism.

Introduction

Iron plays an important role in the formation of both fly ash and deposits in many pulverized-coal-fired boilers. Several authors indicate that iron content is a significant indicator of the slagging propensity of a majority of U.S. bituminous coals, in particular eastern bituminous coals [Bryers, 1976; Raask, 1985]. The pyritic iron content of these coals is shown to be a particularly relevant consideration.

The decomposition of pyrite in combustion environments has been discussed by many authors [Cole, et al., 1987; Groves, et al., 1987; Huffman, et al., 1989; Raask, 1985; Srinivasachar and Boni, 1989; Srinivasachar, et al., 1990; Taneja and Jones, 1984]. These authors describe how pyrite decomposes to form pyrrhotite in inert environments at temperatures of 720-820 K. Pyrrhotite often has no definite crystalline structure and its approximate chemical composition is Fe_7S_8 . Under conditions of even modest heating rates and upon exposure to oxygen, pyrite decomposition products can be highly porous materials [Dunn, et al., 1989]. The decomposition of pyrite to pyrrhotite effects an increase in porosity and some channeling and fragmentation [Baxter, 1990]. Pyrrhotite melts in an inert environment at temperatures between 800 and 1450 K, depending on its mode of preparation. At higher temperatures, pyrrhotite can further decompose to form metallic iron. Both pyrite and pyrrhotite are reactive to oxygen. Pyrites combined with carbon also combust differently, usually more slowly, than pure pyrites. Therefore, the transformations of pyrite inclusions in coal particles during combustion are potentially complex but qualitatively understood.

Our work focuses on the release of iron-containing material from coal during combustion. The mode of occurrence of iron in the coals studied varies from primarily (> 95 %) pyrite to dominantly nonpyritic (sulfates, oxides, and carbonates). Experimental evidence for the release of iron-containing material from coal/char particles leads to a chemical/physical mechanistic interpretation directly related to pyrite decomposition and reaction. Further experiments test the critical aspects of this proposed mechanism and contrast it to vaporization, the more common explanation for this type of data. Finally, reported observations by other investigators are discussed, together with their possible explanation by the same mechanism.

Coal Characterization and Experimental Conditions

The suite of size-classified coals used in these experiments is indicated in rank order in Table 2.1, together with several selected properties. Several different size ranges were used in the experiments with the size-classified coals. More detailed information on the sizes used and the properties of specific size ranges is presented later. Similar information on the suite of utility-grind

coals is indicated in Table 2.2. Note that both suites range in rank from lignite to lv bituminous and include representatives from a wide variety of geographical locations. All are U.S. coals and several are beneficiated. There are also several blends among the coals considered. All of these coals were examined in this work. Detailed data from a few are used to illustrate the major points of the discussion, whereas the remainder of the data are presented in summary form. Additional details on the properties of several of these coals are provided in the detailed discussion of results.

Table 2.1

Characteristic properties of size-classified coals studied during this investigation.

Coal	PSOC # or other	Parr Values*			Ash† [-]	Rank
		Fixed Carbon [-]	Volatile Matter [-]	Heating Value Btu/lb		
Pocahontas #3	1508-D	83.8	16.2	15642	7.4	lv Bituminous
Lower Kittanning	1516-D	81.4	18.6	15488	10.3	lv Bituminous
Pittsburgh #8	1451-D	61.2	38.8	14682	13.7	hv A Bituminous
Pittsburgh #8	EPRI-C2	54.9	45.1	13752	8.7	hv B Bituminous
Pittsburgh #8	EPRI-C1	55.2	44.8	13643	11.8	hv B Bituminous
Kentucky #9	EPRI-MC	54.2	45.8	12939	10.3	hv C Bituminous
SOAP§		57.6	42.4	12900	2.8	hv C Bituminous
Pittsburgh #8	EPRI-RM	54.9	45.1	12867	33.7	hv C Bituminous
Illinois #6	1493-D	57.1	42.9	12832	15.2	hv C Bituminous
Hiawatha	1502-D	55.8	44.2	12678	9.0	hv C Bituminous
Kentucky #9	EPRI-RM	54.6	45.4	12286	15.0	hv C Bituminous
Blue #1	1445-D	52.1	47.9	12107	4.6	hv C Bituminous
Dietz	1488-D	56.1	43.9	10000	5.4	Subbituminous B
Smith-Roland	1520-D	38.0	62.0	9177	12.4	Subbituminous C
Lower Wilcox	1443-D	21.8	78.2	8459	21.4	Subbituminous C
Beulah	1507-D	54.3	45.7	7747	12.5	Lignite A

* Fixed carbon and volatile matter are on dry, *mineral*-free (as opposed to ash-free) basis.

Heating value is on a moist, mineral-free basis.

† Ash is on a dry basis.

§ Spherical Oil Agglomeration Product derived from Illinois #6 coal.

The coals with PSOC ID numbers in Table 2.1 were sampled, size-classified, and stored in inert gas environments to prevent slow oxidation (weathering) of the pyrite with time. Such weathering of pyrite at modest temperatures can occur rapidly, with significant formation of sulfates within a few days [Steger and Desjardins, 1978] and significant rate enhancements from both the presence of moisture in the air and interactions with coal and coal-bound minerals [Shyu, et al., 1981]. The remaining coals were pulverized and stored in various containers with no attempt to prevent oxidation.

Table 2.2

Characteristics of utility-grind coals studied during this investigation.

Coal	Parr Values*			Ash†	Rank
	Fixed Carbon [-]	Volatile Matter [-]	Heating Value Btu/lb		
Pocahantas #3 (1)	85.8	14.2	15712	7.1	lv Bituminous
Upper Freeport [¥]	71.45	28.55	15342	21.66	mv Bituminous
Mingo Logan	64.18	35.82	15141	9.34	hv A Bituminous
Pittsburgh-Seam	59.01	40.99	15154	8.40	hv A Bituminous
Illinois #6 (3)	57.32	42.68	15023	5.62	hv A Bituminous
Pittsburgh #8 (2)	61.51	38.49	14843	6.55	hv A Bituminous
Massey Sprouce	62.85	37.15	14786	8.33	hv A Bituminous
Eastern Kentucky	59.76	40.24	14724	10.15	hv A Bituminous
Pittsburgh #8 (1)	56.44	43.56	14695	10.68	hv A Bituminous
Utah Blind Canyon	51.92	48.08	14276	10.40	hv A Bituminous
Kentucky #11 [¥]	57.38	42.62	13269	22.21	hv B Bituminous
Illinois #6 (2)	56.34	43.66	13083	12.33	hv B Bituminous
SOAP [§]	57.6	42.4	12900	2.8	hv C Bituminous
Kentucky #9 [¥]	57.15	42.85	12791	14.64	hv C Bituminous
Hanna Basin	57.59	42.41	12053	11.05	hv C Bituminous
Illinois #6 (1) [¥]	55.68	44.32	11997	10.13	hv C Bituminous
Roland-Seam	52.85	47.15	11494	6.29	Subbituminous A
Decker	53.92	46.08	10726	5.11	Subbituminous A
Black Thunder	42.27	57.73	10675	6.46	Subbituminous A
Belle Ayr	49.02	50.98	10130	6.04	Subbituminous B
Wyodak	51.79	48.21	10059	6.22	Subbituminous B
Antelope	54.53	45.47	9918	5.51	Subbituminous B
Eagle Butte [¥]	51.68	48.32	9286	6.40	Subbituminous C
Beulah Lignite [¥]	51.28	48.72	8202	13.86	Lignite A
Texas Lignite [¥]	39.98	60.02	7513	51.96	Lignite A
Blends					
Eastern Blend	67.77	32.23	15312	8.67	hv A Bituminous
Pitt. #8/Decker	61.3	38.7	13599	6.96	hv B Bituminous
NIPSCO Blend (1)	54.3	45.7	12786	7.71	hv C Bituminous
NIPSCO Blend (2)	53.26	46.74	12742	7.80	hv C Bituminous
Roland/Illinois #6	54.3	45.7	12467	8.97	hv C Bituminous
Eagle Butte/Ken. #9	51.3	48.7	10592	9.39	Subbituminous A

* Fixed carbon and volatile matter are on dry, *mineral-free* (as opposed to ash-free) basis. Heating value is on a moist, mineral-free basis.

† Ash is on a dry basis.

§ Spherical Oil Agglomeration Product derived from an Illinois #6 coal.

¥ Coals obtained from PSIT as part of the original suite used in their mineral investigations.

In all cases, samples of the coals were analyzed at several stages of experimentation to determine the fraction of pyritic iron.

In the experiments, coal samples are entrained in a laminar flow reactors in the Sandia Coal Devolatilization Laboratory (CDL) and the Coal Combustion Laboratory (CCL) and in the turbulent flow of the Multifuel Combustor (MFC). In all cases, particularly reacted solids are sampled at various stages of burning using helium-quench sampling probes. Schematic diagrams these reactors and their sampling systems are presented in Figures 2.1 - 2.5. The CCL is an up-fired reactor that uses a vitiated flow as the entrainment fluid for the particles. The CDL reactor is similar in design to the CCL except that it is down-fired and uses electrically heated inert entrainment gases (N₂) rather than a vitiated flow. Both the CCL and the CDL are relatively short residence time facilities (< 300 ms) that entrain size-classified particles in a dilute stream with the gases. The MFC is a down-fired, pilot-scale combustor with longer residence time capabilities (0 - 5 s), comparable to or in excess of those achieved in commercial-scale equipment. In these experiments, the utility grind coal was fired in the MFC at rates (gms/cm² sec) similar to those achieved in commercial-scale operations. Further details of the reactors and their diagnostics are available elsewhere [Baxter, 1992; Baxter and Mitchell, 1992; Fletcher, 1989].

Elemental ash analyses are obtained for each of the solid samples. The inorganic elements in samples from the CDL and CCL were analyzed by Coors Analytical Laboratories using an inductively coupled plasma (ICAP) according to ASTM Procedure D 3682 with the following revisions: (1) a lithium metaborate and lithium tetraborate flux was used for the fusion, and (2) concentrations are determined using the ICAP. Samples from the MFC were analyzed by the chemical analysis laboratories of CONSOL Inc., Library, PA, using the standard ASTM Procedure (D 3682).

Loss of any particular element from the coal and char particles can be determined from elemental analyses of their inorganic material and a knowledge of the overall particle mass loss by the following equation:

$$f_i(t) = \frac{x_i(t)}{x_i(0)} \frac{m(t)}{m(0)} \quad (2.1)$$

The variable f represents the total mass of any constituent of the particle (in this case iron), normalized by its original mass. The variable x represents the mass fraction of that constituent in the particle at residence time t . The variable m represents the total particle mass. The subscript i is an index for the various inorganic elements. Time-dependent values and initial values are indicated by t and 0 as independent variables, respectively.

Elemental analyses of the unreacted sample and the sample of the raw material provide the information required to compute the first fraction in Equation 2.1. Both "tracer" and, where possible, mass balance techniques allow estimations of the second fraction, i.e., the residual particle mass. Only the CCL provides a capability to determine overall mass loss by an experimentally determined mass balance. Residual mass of the particles in this reactor is

Figure 2.1 Schematic diagram of the laminar flow reactor, in Sandia's Coal Combustion Laboratory (CCL), used in these experiments. Coal particles entrained in the hot, vitiated gas flow upward as they proceed through the stages of heat-up, devolatilization and heterogeneous oxidation.

Figure 2.2 Schematic diagram of the laminar rapid-quench sampling system used in these experiments in each of the coal reactors. The openings in the filter are $1\text{ }\mu\text{m}$ in diameter.

Figure 2.3 Schematic diagram of the laminar flow reactor, in Sandia's Coal Devolatilization Laboratory (CDL), used in these experiments. The reactor is down-fired and uses electrically heated inert gas as the entrainment medium.

Figure 2.4 Schematic diagram of an aerodynamic, sample-separation portion of the sampling system associated with the CDL. Solids and vapors (tars) are separated in flight in the sampling system.

Figure 2.5 Schematic diagram of the Sandia Multifuel Combustor. A sampling system similar to that illustrated in Figure 2.2 is used with the MFC.

determined both by calculating the ratio of mass of coal fed to mass of char collected and by a tracer technique. Agreement between the two techniques is excellent so long as appropriate tracers are chosen.

Any element that does not leave the particles during reaction may be used as a tracer. The residual mass is determined from a tracer as follows:

$$\frac{m(t)}{m(0)} = \frac{x_i(0)}{x_i(t)} \quad (2.2)$$

where subscript j identifies a tracer. Note that the precision of the measure of residual particle mass depends on the precision of the tracer measurement in the raw coal. Promising candidates for tracers include silicon, aluminum and, in some cases, titanium [Baxter, et al., 1993]. The independent analysis of all three of these quantities provides a cross check of the data and allows determination of statistical confidence intervals. A mass balance technique, i.e., the ratio of mass collected to mass fed in the reactor, allows a fourth independent measure of overall mass loss.

The overall mass loss ($1-m/m_O$) estimated by a tracer using Equation 2.2 will be low if a portion of the tracer is lost from the sample during the experiment. Two provisions prevent data from bias of this type in these experiments. First, the tracers selected for these experiments occur in significantly different modes and as different size grains in the coal. The silicon and aluminum occur in the form of silica or silicate grains in the coal matrix. The size distributions of these grains have been measured as a function of burnout, with mineral grain sizes in the raw coal on the order of 5-10 μm [Baxter, 1990]. The titanium, on the other hand, is more homogeneously dispersed through the coal and typically occurs in smaller size grains. Some of the titanium is also atomically dispersed. It is unlikely that mineral species, with such differences in size and mode of occurrence in the coal, are sensitive to the same types of evolution processes.

The second provision against systematic bias of the data involves the comparison between the results of the mass balance and tracer techniques. Inorganic species used as tracers may be lost from the coal or char particle during combustion but cannot systematically be added to the coal. Therefore, the tracer techniques will bias the estimate of m/m_O to higher values, if at all. On the other hand, a value of m/m_O determined from a mass balance on the reactor may be too low, due to sample lost from the collection system. However, the mass balance technique cannot systematically overestimate the overall mass loss. Therefore, the two techniques will be biased in opposite directions, if at all. Agreement between the results from the two techniques provides a reasonably rigorous test of both the precision and accuracy of the m/m_O values.

Results and Discussion

Fuel Characterization

The fuel on which the initial experiments focus is a hva bituminous, Illinois #6 coal (PSOC-1493d). Size- and aerodynamically-classified samples of this coal in two size ranges (75-105 μm and 106-125 μm) are involved in the experiments. The elemental mass fractions of the inorganic constituents of these two size fractions of the coal appear in Table 2.3 as oxide percents. The values in the table represent averages and coefficients of variation from two to eight replicate measurements for each size class. Total ash content was also measured independently of the elemental ash composition. This measured result is presented together with the sum of the oxides in the table. The total ash content is typically higher than the sum of the elemental components, with the difference representing unmeasured species. Sulfur is the largest contributor to these unmeasured species.

Table 2.3

Elemental analysis of the inorganic constituents of size-classified samples of Illinois #6 coal.

Oxide	75-106 μm Fraction		106-125 μm Fraction	
	Mean	Coefficient of Variation	Mean	Coefficient of Variation
	(mass %)	(-)	(mass %)	(-)
SiO ₂	3.61	0.061	4.23	0.140
TiO ₂	0.088	0.042	0.092	0.102
Fe ₂ O ₃	4.2	0.137	3.55	0.162
Al ₂ O ₃	1.43	0.049	1.68	0.123
CaO	0.70	0.206	0.56	0.382
MgO	0.011	2.00	0.110	0.334
Na ₂ O	0.096	0.208	0.039	0.336
K ₂ O	0.18	0.310	0.14	0.640
Ash				
(sum)	10.31	—	10.40	—
(measured)	11.83	0.112	11.85	0.174

Elemental compositions of the ash of the two size fractions differ in the amount of magnesium, calcium, sodium, potassium, iron, aluminium, silicon, and titanium, in that order. The differences in the mineral compositions are sufficiently large that the two size fractions are treated separately in the analysis of the data.

The variation in measured iron content is large compared with other major components of the ash. This large variation must be recognized when interpreting the results of experiments. Analysis of the sulfur forms in this coal indicates that essentially all (> 95 %) of the iron is originally bound as pyrite. Silicon, aluminum and titanium are the most precisely determined ash species in these experiments, as indicated by the coefficient of variations. Four replicated samples were used in determining all of the compositions for the 75-106 μm size fraction. At least six replicates were used in determining the silicon, aluminium, titanium and iron compositions of the 106-125 μm coal particles. Four replicated measurements were performed for the remaining elements except magnesium, for which two measurements were obtained. All of these measurements were performed in the same laboratory by the same technique. Additional measurements were obtained at other laboratories with these samples and by other investigators using very similar samples of the same coal. These additional data are not used in analyzing the results of our experiments due to relatively high laboratory-to-laboratory variations in the results.

Accuracy and consistency of the CDL- and CCL-derived chemical analyses are monitored by periodic analysis of NIST standard coals. Results for the 22 analyses of the NIST standard coals completed during the course of this project are summarized in Table 2.4 for the eight major elements common to coal ashes. Both the accuracy and precision of the measurements are relevant

to our results. The precision is arguably more significant than the accuracy and is indicated by the standard deviation and the coefficient of variation (standard deviation divided by the mean). As is indicated in the table, the standard deviation is less than 5 % of the mean for all components except titanium, which is 5.5 %. The accuracy is indicated by the ratio of the average measured value to the certified value in the standard. The average measured values of the components most relevant to this investigation (Si, Al, Ti, and Fe) are all within 5 % of the certified value. These data provide a traceable path between our measurements and certified NIST standards.

The chemical analysis laboratories of CONSOL Inc. analyzed all samples derived from the MFC. These analyses benefit from the coal-specific optimized procedures used by CONSOL. All samples were done in duplicate, with the average of the two measurements reported. Every third sample is a NIST-traceable standard and is used as the basis for calibration of the instrument. The accuracy and precision of the elemental compositions so analyzed are approximately ± 3 % of the measured values.

Based on these results and statistical analysis of the data, trends in data from both the small scale reactors (CDL and CCL) and the MFC are shown to significantly exceed measurement uncertainty with respect to chemical analysis. Uncertainty introduced by experimental techniques is also quantified and shown to be small compared to trends observed in the data. These results also indicate that the variations in measured initial concentrations of the samples, as indicated in Table 2.3, are usually dominated by true sample-to-sample variation rather than chemical analysis error.

Table 2.4

Experimentally determined composition of the inorganic constituents of a NIST standard coal (NBS 1632b) compared with the certified values.

Oxide	Laboratory Results		NIST Certified Values	
	Mean (mass %)	Coefficient of Variation (-)	Mean (mass %)	Ratio of Lab to Standard (-)
SiO ₂	2.95	0.042	3.00*	0.98
TiO ₂	0.0724	0.055	0.076	0.95
Fe ₂ O ₃	1.05	0.048	1.09	0.96
Al ₂ O ₃	1.62	0.036	1.615	1.00
CaO	0.282	0.154	0.26	1.08
MgO	0.0627	0.198	0.064	0.98
Na ₂ O	0.0656	0.326	0.069	0.95
K ₂ O	0.0755	0.470	0.09	0.84

* The value for silicon is reported by NIST but not certified.

Overall Mass Loss

Figure 2.6 illustrates typical (m/m_0) data obtained during these experiments. The data are tightly grouped, with no large and consistent differences between the results of the various analyses. A detailed examination indicates that the titanium results are consistently different from the others for reasons discussed in detail elsewhere [Baxter, et al., 1993]. For our purposes, however, the results are in sufficient agreement. Similar data were obtained for each particle size range and each gas environment.¹ Table 2.5 summarizes all of the m/m_0 data for this coal and reports mean values (μ), standard deviations (σ), and confidence intervals for the mean values. In general, the value of m/m_0 is determined within 5-10 absolute percent at a 95 percent confidence level. Note that the confidence intervals are for the mean value of m/m_0 , not an indication of the range of variation among the m/m_0 values.

Figure 2.6 Typical mass loss data obtained during experiments in the CCL. These data are for the 106-125 μm particles in the 6 mole percent oxygen environment. In general, overall mass loss (m/m_0) is determined within about 4 percent.

¹Systematic errors in the mass balance technique were observed for two data points (47 and 72 ms) in the 6 % oxygen environment for the 75-106 μm particles. Therefore, these data were not used in the overall data analysis. Elimination of these data has no impact on the qualitative results and only a minimal impact on the quantitative results.

Table 2.5
Overall mass loss data and confidence intervals as a function of residence time for
both particle size ranges and both gas environments.

τ^a	μ	σ	95 % Confidence	99 % Confidence
(ms)	(-)	(-)	Interval (+/-) (-)	Interval (+/-) (-)
75-106 μm size Fraction				
6 % Overall Oxygen Concentration				
0.0	1.0	0.0	0.0	0.0
47.0	0.35	0.007	0.061	0.307
72.0	0.31	0.002	0.022	0.109
95.0	0.28	0.006	0.052	0.260
117.0	0.26	0.002	0.002	0.005
12 % Overall Oxygen Concentration				
0.0	1.0	0.0	0.0	0.0
47.0	0.39	0.012	0.015	0.025
72.0	0.31	0.032	0.080	0.185
95.0	0.22	0.005	0.013	0.030
117.0	0.15	0.010	0.026	0.059
106-125 μm size Fraction				
6 % Overall Oxygen Concentration				
0.0	1.0	0.0	0.0	0.0
47.0	0.47	0.021	0.053	0.122
72.0	0.43	0.025	0.061	0.142
95.0	0.40	0.054	0.133	0.307
117.0	0.36	0.029	0.072	0.166
12 % Overall Oxygen Concentration				
0.0	1.0	0.0	0.0	0.0
47.0	0.48	0.022	0.055	0.126
72.0	0.34	0.034	0.084	0.193
95.0	0.25	0.028	0.029	0.045
117.0	0.20	0.022	0.056	0.129

^a Based on measured velocities of a 100 μm particle.

Iron Loss

These data and the elemental analysis of iron in the char particles provide the information required in Equation 2.1 to estimate the amount of iron released from the coal. Figure 2.7 shows the results of such an analysis for particles from the 106-125 μm size fraction in the 6 percent oxygen environment (top) and the 12 percent oxygen environment (bottom). These data indicate a large and rapid depletion of iron in the char immediately after coal devolatilization, but before significant char oxidation. Approximately 45 percent of the total original iron in the coal particle leaves over this 25 ms time period. The statistical analysis of all of the experiments performed with the large particles is reported in Table 2.6. The small particle data are discussed later.

Table 2.6
Iron evolution data, with confidence intervals, for the 106-125 μm size fraction of the Illinois #6 coal in both gas environments.

τ^a	μ	σ	95 % Confidence	99 % Confidence
(ms)	(-)	(-)	Interval (-)	Interval (-)
106—125 μm size Fraction				
6 % Overall Oxygen Concentration				
0.0	1.0	0.0	1.0—1.0	1.0—1.0
47.0	0.91	0.160	1.0—0.77	1.0—0.70
72.0	0.57	0.101	0.66—0.48	0.70—0.43
95.0	0.48	0.102	0.58—0.37	0.64—0.31
117.0	0.54	0.086	0.63—0.46	0.68—0.41
12 % Overall Oxygen Concentration				
0.0	1.0	0.0	1.0—1.0	1.0—1.0
47.0	1.10	0.175	1.0—0.93	1.0—0.84
72.0	0.48	0.196	0.57—0.39	0.63—0.34
95.0	0.56	0.202	0.66—0.46	0.60—0.29
117.0	0.59	0.175	0.70—0.48	0.76—0.42

^a Based on measured velocities of a 100 μm particle.

The data in Table 2.3 show the magnitude of variations in measured iron content of the raw coal. The nonzero confidence intervals shown at a residence time of 0 ms in Figure 2.7 reflect this variation. Both imprecision in the measurement and actual sample-to-sample variation in the iron content contribute to this variation. The detection limit for iron by this analysis technique is 0.001 weight percent, which is equal to or lower than the detection limits for the species being used as tracers. In addition, data for each single sample are closely grouped. Therefore, the variability in measured iron content shown in Table 2.3 and at 0 ms in Figure 2.7 are apparently due to actual sample-to-sample variation rather than to imprecise experimental technique. This sample-to-sample variation in iron content is also the likely cause for the indicated increase in average iron content indicated in Table 2.6 in the 12 % oxygen environment at a particle residence time of 47 ms.

Figure 2.7 Iron loss data for the 106-125 μm diameter particles. Data from both the 6 mole % oxygen (a) and 12 mole % oxygen (b) environments in the CCL are shown. The large decrease in iron seen at about 50 ms residence time in both environments corresponds to the incipient stages of oxidation, when the coal particles are first exposed to oxygen.

These sample-to-sample variations in the iron content of the particles persist despite our efforts to homogenize the fuel through size and aerodynamic classification. A comparison of the trends illustrated in Figure 2.7 with the uncertainty in the measurement (due to all sources, including sample-to-sample variations) is somewhat complicated since the various means of calculating the iron loss (f_i) are not entirely independent. All depend on the same measure of iron in the coal sample. The variance in the value of f can be estimated as a function of residence time by standard techniques using the measured coefficients of variation from Table 2.3. The variance of f is approximated by the variance of each of its components as follows [Papoulis, 1984]:

$$\sigma_{f_i}^2 = \sigma_{m/m_o}^2 \left(\frac{\partial f_i}{\partial m/m_o} \right)^2 + \sigma_{x_i}^2 \left(\frac{\partial f_i}{\partial x_i} \right)^2 + \sigma_{x_o}^2 \left(\frac{\partial f_i}{\partial x_o} \right)^2 \quad (2.3)$$

The three right-hand terms represent the contributions from uncertainty in: (1) the overall mass loss, (2) the amount of element i (in this case iron) in the sample, and (3) the amount of element i in the raw coal, respectively. The indicated variances (σ^2) in the equation are taken from Table 2.3 directly for the last and first terms, respectively. The variance in the second term is calculated from the coefficient of variation in Table 2.3, accounting for the change in the overall iron content of the sample. If the measured standard deviations in iron measurements are smaller than the 95 % confidence intervals of the chemical measurement technique itself, the latter, more conservative number, is used in its place. The indicated derivatives are evaluated at the mean values of the variables x_i , x_o , and m_i/m_o . Equation 2.3 becomes

$$\sigma_{f_i}^2 = \sigma_{m/m_o}^2 \left(\frac{\langle x_i \rangle}{\langle x_o \rangle} \right)^2 + \sigma_{x_i}^2 \left(\left\langle \frac{m_i}{m_o} \right\rangle \frac{1}{\langle x_o \rangle} \right)^2 + \sigma_{x_o}^2 \left(\left\langle \frac{m_i}{m_o} \right\rangle \frac{\langle x_i \rangle}{\langle x_o \rangle^2} \right)^2 \quad (2.4)$$

where σ_m represents the variance of measurement m , angle brackets represent mean values, and the remaining terms have been previously defined. Calculation of the variance allows computation of the confidence intervals. The resulting confidence intervals for the data in Figure 2.7 are shown in Table 2.6.

Use has been made of the physical bounds on the function f ($0 \leq f(t) \leq 1.0$) in compiling Table 2.6. Table 2.6 confirms that the observed trends shown in Figure 2.7 are larger than the uncertainty in the data. Clearly, a significant fraction of the iron in the coal is released from the coal particles during the 25 ms immediately after devolatilization. The iron is apparently released either as a volatile compound or in the form of a fine particulate fume that is small enough to pass, uncollected, through the filter in the sampling line. As will be shown below, there is compelling evidence that, in fact, the released iron is one component of a fine particulate fume.

Iron dominates the total amount of mineral evolved from this coal in these experiments. Figure 2.8 illustrates the composition of the original coal minerals on an elemental basis and the fraction of each which evolves from the particle in a typical experiment. Sulfur is excluded from

this plot due to the complexity of characterizing the interactions of organic and inorganic sulfur during combustion. Over 80 mass percent (on an elemental basis) of the evolved mineral consisted of iron. These results are from a single experiment. There are random variations in the data that are indicated as small amounts of loss of other inorganic constituents. The small amount of aluminium mass loss indicated in the figure is an example of one such result. In general, there is no indication of any loss of aluminium or silicon during these experiments.

Figure 2.8 Typical elemental compositions of the residual and evolved coal minerals. Data are for particles at 117 ms residence time in an environment with 6 mole percent bulk oxygen concentration in the CCL.

Additional iron-release data for this coal, i.e., those for the 75-106 μm particles, are presented in Fig. 2.9 and Table 2.7. The same basic trend is seen in these data, with a large release of iron immediately after coal devolatilization, during the incipient stages of combustion. A more detailed discussion of these data is included after the presentation of a proposed mechanism for this iron release and in the context of testing the predictions of that mechanism.

Figure 2.9 Iron loss data obtained for the 75-105 μm diameter particles. Data from both the 6 mole % oxygen (a) and 12 mole % oxygen (b) environments in the CCL are shown.

Table 2.7
Iron evolution data, with confidence intervals, for the 75—106 μm size fraction
of the Illinois #6 coal in both gas environments.

τ^a	μ	σ	95 % Confidence	99 % Confidence
(ms)	(-)	(-)	Interval (-)	Interval (-)
75—106 μm size Fraction				
6 % Overall Oxygen Concentration				
0.0	1.0	0.0	1.0—1.0	1.0—1.0
47.0	0.61	0.090	0.80—0.42	1.00—0.16
72.0	0.53	0.077	0.69—0.36	0.91—0.14
95.0	0.44	0.064	0.58—0.30	0.76—0.12
117.0	0.41	0.059	0.51—0.32	0.58—0.24
12 % Overall Oxygen Concentration				
0.0	1.0	0.0	1.0—1.0	1.0—1.0
47.0	0.65	0.098	0.81—0.50	0.94—0.37
72.0	0.59	0.106	0.82—0.35	1.00—0.04
95.0	0.45	0.066	0.59—0.30	0.78—0.12
117.0	0.49	0.060	0.62—0.36	0.80—0.18

^a Based on measured velocities of a 100 μm particle.

Mechanistic Interpretation

The release of most inorganic species from coal particles traditionally is explained as a process of local reduction followed by vaporization [Neville, et al., 1980; Quann, et al., 1982; Quann and Sarofim, 1982; Senior and Flagan, 1984; Wibberley and Wall, 1986], although some authors specifically reject this idea for iron-containing species [Raask, 1985]. The suitability of the vaporization mechanism as an explanation for the data obtained in our work is investigated as follows. If we assume a constant diameter sphere undergoing pseudo-steady vaporization and reaction in a quiescent medium, the total rate of iron vaporization from the sphere should be given by

$$N_f = h_f \theta A (x_s - x_b) + x_s \sum_{i=1}^n N_i \quad (2.5)$$

where N_f is the molar transfer rate of iron from the particle, h_f is the mass transfer coefficient, θ is the blowing factor, A is the particle surface area and x is the mole fraction of iron at the surface (subscript s) and in the bulk phase (subscript b). This expression can be evaluated for the

vaporization of elemental iron under the most favorable conditions for this vaporization as follows. The mass transfer coefficient can be derived from a Sherwood number correlation and the diffusion coefficient of iron in the gas phase. The mole fraction of iron at the surface can be approximated as a function of temperature from a vapor pressure curve and the mole fraction in the bulk phase will be considered negligible.

The following observations and approximations allow quantitative evaluation of N_f . The peak measured particle temperatures during the iron release were about 1710 K (average particle temperature is 1688 K) in the 6 % oxygen environment. Assuming a 100 μm sphere at the peak temperature, the mass transfer coefficient is about 0.40 mol/cm²-s, the vapor pressure of iron is about 6.1×10^{-6} atm, and the sum of the molar fluxes (from the data in Table 2.5) is 7.87×10^{-8} mol/s. These values assume metallic iron is the vaporizing species and the remainder of the mass lost from the coal particle is carbon. The predicted total molar transfer rate is 2.5×10^{-11} mol/s. A reasonable upper bound on the rate of vaporization corresponds to the entire particle surface being covered with iron, in which case the transfer rate is about 7.8×10^{-10} mol/s. The observed transfer rate is much higher, i.e., over 7.1×10^{-9} mol/s.

There are several simplifying assumptions in the above discussion that merit more careful examination. Coal particles are not spherically symmetric (see Fig. 2.10 below), nor are the mineral grains homogeneously distributed throughout the coal. A theoretical discussion of vaporization from isolated mineral grains in coal particles is available in the literature [Quann and Sarofim, 1982] and can be used to indicate the consequences of explicitly considering the granular nature of the mineral grains. This study shows that, for inorganic material that occurs as discrete mineral grains, such as pyrite and its decomposition products, "internal diffusion resistance [to mass transfer] will dominate and that the partial pressure...at the surface will be orders of magnitude less than the equilibrium value at the inclusions." The study shows that the rate of vaporization indicated above corresponds to the maximum possible rate and is likely to be orders of magnitude higher than the actual rate for discrete mineral grains.

There remain significant assumptions about spherical symmetry, chemical reactions by the vapors, etc. To consider the implications of these assumptions is a complicated theoretical task. We turn rather to the experimental observation that the iron release occurs at rates far in excess of more volatile and more plentiful components such as silica. According to standard references [Perry, et al., 1984], the vapor pressure of metallic iron is lower than that of silicon or any of its oxide derivatives. The fact that essentially no silicon was observed to leave the particles, even though they experience the same experimental conditions as the iron, is an indication of the inadequacy of vaporization as an explanation for these data, independent of any theoretical considerations. However, the silicon vapor pressure data in standard reference texts [Perry, et al., 1984; Weast, 1976] is in significant disagreement with similar data from other reliable sources [Chase, et al., 1985; Lankford, et al., 1985]. Until these discrepant data are resolved, it is not clear whether silicon loss could be expected to be greater or less than iron loss by vaporization.

There are several iron-containing species more volatile than metallic iron which should be considered. Iron carbonyls are among the most well-known of these. However, iron pentacarbonyl, the most stable iron carbonyl, decomposes at low temperatures (300-500 K) and is difficult to form from stable iron-containing compounds. Ferrous and ferric chloride are both quite

volatile. But, there is insufficient chlorine in this coal to account for the loss of iron by the formation and vaporization of these compounds. There are a few organo-metallic compounds which have also been considered. These are not necessarily more volatile than metallic iron and are unstable at high temperatures. Furthermore, the decomposition of pyrite at high temperatures is reasonably well understood and involves no volatile intermediate species. On the basis of these analyses and observations, we conclude that the iron is not being released through a mechanism of vaporization under these combustion conditions.

We postulate an alternative mechanism for this iron release from the coal. This is illustrated conceptually in Figure 2.10. In this figure, a pyrite grain is shown imbedded in a coal particle. The pyrite is nearly as reactive to oxygen as is coal or coal char. However, during the early combustion history of the particle the coal volatiles evolve and consume the local oxygen. Sulfur is emitted simultaneously from the pyrite as it decomposes to pyrrhotite. At the end of coal devolatilization, the pyrite particles have been converted to pyrrhotite, which is also very reactive to oxygen. As the oxygen-depleted volatile cloud separates from the coal particle, the pyrrhotite grains are exposed to oxygen. It is at this point that the large decrease in iron is observed (see Figure 2.7, for example). This suggests that the chemical reactivity of pyrrhotite to oxygen is related to the evolution of iron.

We postulate that an iron fume is formed as a consequence of this chemical reactivity and that some portion of the fume is convected away from the particles during the early stages of char oxidation.

Verification of Mechanism

Several further experiments were conducted to verify and add detail to this postulated mechanism. Scanning electron micrographs of the coal particles were obtained at each stage of burning. These micrographs, shown in Fig. 2.11, show that the pyrrhotite grains are very porous prior to the loss of iron. Fig. 2.11a is taken from the 106-125 μm particles collected at 47 ms residence time in the 6 percent oxygen environment. A closer examination of the same particles (Fig. 2.11b) reveals the porous nature of the particles, being composed of small nodules, 0.1 μm or less in diameter, loosely bound together to form the larger pyrrhotite grain. After the loss of iron, the original grains appear to have disintegrated (Fig. 2.11c). The micrograph illustrated in Fig. 11c is taken from the 106-125 μm particles collected at 72 ms residence time in the 6 percent oxygen environment. Figure 2.11d illustrates a micrograph from the same sample, but at higher magnification. The top portion of the mineral grain in this micrograph is composed primarily of silicon and aluminium and shows no indication of disintegration. The bottom half is iron-rich and appears to have fragmented. The very small particles littering the surface of the char are also iron-rich and are examples of fume particles generated by the disintegration of the larger mineral grain. Both convection by the products of heterogeneous char combustion and thermophoretic forces on the fume particles in the thermal boundary layer will tend to transport much of this fume away from the particle. These submicron fume particles are sufficiently small so that they pass through the nominal 1 μm openings in the filter without being collected in the sampling system.

Figure 2.10 Conceptual diagram of the mechanism of iron evolution postulated on the basis of our experiments. The iron is released as a particulate fume as the porous pyrrhotite grains react with oxygen and disintegrate.

Figure 2.11a,b Scanning electron micrographs of (a) a char particle with included pyrrhotite grains immediately before iron evolution, (b) the detailed structure of the pyrrhotite grain. Compare with Fig. 2.11c on next page.

Figure 2.12 Forms of iron-containing mineral species in the coal samples as a function of residence time in (a) the 6 mole % oxygen environment and (b) the 12 mole % oxygen environment in the CCL experiments.

The data from experiments with smaller particles also show that this postulated mechanism correctly predicts trends in iron release rates that are opposite to those predicted by a vaporization mechanism. The postulated mechanism depends on the presence of an oxidizing environment in the vicinity of the pyrite/pyrrhotite grain whereas vaporization depends on the existence of a locally reducing environment. A larger fraction of the volume of a small particle is exposed to oxygen than for a large particle under similar conditions of temperature and oxygen concentration. Therefore, repeating the experiments with smaller particles should produce trends in the data that distinguish a vaporization process from a heterogeneous reaction process. Figure 2.9 shows the results of an experiment in which smaller (75—106 μm diameter) coal particles were entrained in the same environments. The *extent* of iron loss is expected to increase if the mechanism proceeds through a chemical reaction with oxygen whereas it should decrease if it proceeds through vaporization. However, the small particles have a greater total exterior surface area than the large particles. Therefore, the *rate* of iron loss is expected to increase by both mechanisms as particle size decreases.

Oxygen penetration in the particles can be approximated using the Thiele modulus description of intrinsic reaction [Satterfield, 1970]. In this case, the global reaction rate coefficients and oxygen dependence were inferred from the particle temperature and solid sample data. Particle apparent density, void fraction, and N_2 BET surface area were measured at 0.32 g/cc, 0.810, and 55 m^2/g , respectively. Under the conditions of these experiments, the ratio of the effectiveness factor of the small particles (90 μm) to that of the large particles (115 μm) varies from 1.4 to 1.5, depending on the assumed value of the tortuosity factor. Therefore, changing the particle size fraction in the reactor could be expected to increase the effect of oxygen on the intrinsic reactions by a factor of 40 to 50 percent. This increased oxygen penetration should produce a measurable change in the iron loss data.

The results of these experiments, shown in Figure 2.9, illustrate that the extent of iron loss increases as coal particle size decreases, consistent with the mechanism of chemical reaction as an explanation for the loss of iron. Table 2.7 lists the means, standard deviations and confidence intervals for the data shown in Figure 2.9. The 95 % confidence intervals of these data exclude those of the data for the larger particles at the latest residence times in both gas environments. Time required to heat and devolatilize the particles also decreases due to smaller particle mass. The overall mass loss for these data are reported together with the larger particles in Table 2.5.

These data support the proposed mechanism of iron release through chemical reaction and provide additional details of the process. The porous pyrrhotite grains appear to disintegrate as they react with oxygen, freeing the small nodules of the grain. Many of these small nodules adhere to the coal particle, while others are carried away from the coal particle with the products of heterogeneous combustion of the coal char or by thermophoresis. Those which are carried into the bulk gas stream become the iron oxide/sulfide fume which passes through the filter. However, they do not become vapors during the process. They are emitted as small (up to 0.8 μm) solid particles.

The sampling system used in the CDL was used in the CCL to allow the fine particulate to be collected. Micrographs of the collected material are illustrated in Figure 2.13, together with energy

dispersive spectra of the particles (coated with gold to enhance the signal) and the filter. Note that potassium and iron are the only two species in appreciable concentration in the particulate. The presence of potassium is attributed to either vaporization or release during devolatilization. The latter mechanism is discussed elsewhere [Baxter, et al., 1993]. Sulfur is also present, but it is masked by the signal from the gold coating. There is no iron signal from the filter itself. Closer examination of the particles indicates that they are approximately 0.5 μm in diameter and appear to have significant porosity.

Figure 2.13 SEM photograph of iron fume particles captured in the gases from size-classified (106-125 μm) Illinois #6 coal particles. The micron-sized fume particles are composed principally of potassium, sodium, and iron.

The remaining coals indicated in Tables 2.1 and 2.2 were examined to determine the extent of iron loss during combustion. Representative results for the coals tested in both the CCL and CDL are presented in Fig. 2.14. The coals illustrated range from lignite to lv bituminous and are arranged in rank order. The iron loss correlates reasonably well with the amount of pyritic iron in the coal. The pyritic iron contents are determined by performing a mass balance on measured pyritic sulfur contents and are measured both before and after the experiments. Note that, even under nitrogen storage, the pyrite oxidizes significantly in essentially all coals. All data shown in Figure 2.14 are from the CCL and represent the average of several runs under conditions of different particle size (45 to 125 μm) and oxygen concentration (6 to 12 %). In the inert environment of the CDL, no iron release was observed. The CDL operates at a significantly lower temperature than the CCL (maximum T_g is 1250 K), in addition to being an inert flow facility.

Figure 2.14 Summary of iron release as a function of coal rank and of pyritic iron content.

Sensitivity of Results to the Extent of Weathering

The presence of iron in submicron particulate has been observed by several investigators. A reasonably comprehensive study of this type was conducted by Quann and Sarofim [Quann and Sarofim, 1982], in which iron enrichment was observed in much the same pattern. Enrichment of iron in the submicron fume compared to the bulk coal greatly exceeds that of other reasonably refractory materials such as, for example, silicon. Similar results are reported by other investigators for a narrower range of coals (discussed later). Most of the other species observed in the fume could be described as products of ash vaporization. The iron results were presented without further discussion. We believe the results can satisfactorily be described in terms of the above mechanism.

However, these investigators and others typically see lower absolute amounts of iron in the fume than have been observed in this study, even though the enrichment factors are high. A possible explanation for the differences in the amount of iron released as a fume between these several investigations is the role of weathering on the release of an iron fume.

Experiments have been conducted in two parts to indicate the extent of coal weathering on iron fume formation. First, the extent by which exposure of coal to room air at room temperature might oxidize the pyrite was investigated. Three utility grind coals originally containing 100 percent pyritic iron [Boni, et al., 1990] were reanalyzed after short (approximately one week) exposure to room temperature air. Figure 2.15 illustrates the fraction of pyritic iron in the coals before (raw) and after (weathered) exposure to air. Pyritic iron content of all three coals decreased to approximately 60 percent. Further similar exposure of the coals to air produced an additional 4 to 5 percent decrease. Thus the initial oxidation of pyrite proceeds much more rapidly than the later oxidation. Our hypothesis is that the surface of the pyrite grains is rapidly oxidizing and producing a sulfated layer. This sulfate layer inhibits the further oxidation of the remaining pyritic iron.

Figure 2.15 Decrease in pyritic iron content with exposure of pulverized coal to air at room temperature for approximately one week for three coals.

The sulfate layer formed on pyrite grains during exposure to air likely impedes the formation of the iron fume under combustion conditions. Combustion tests in the MFC were conducted to evaluate this hypothesis. The first objective was to determine the extent of fume formation from the weathered coal and compare this to the fume formed from the raw coal. The utility grind Illinois #6 coal on which the data in Fig. 2.15 are based is reasonably similar to the size-classified Illinois #6 coal (PSOC-1493d) with the important exception of overall iron content. The former

was selected as the test fuel for these experiments. The ash compositions of these two coals are indicated in Tables 2.8 and 2.9. In these experiments, no formation of the iron fume was detected, in contrast to experiments previously reported which used the unweathered coal. These results are illustrated in Fig. 2.16.

The second phase of these experiments involves exposure of samples of the unweathered coal to air for three days and one week to see if the iron fume previously observed is affected. These experiments will be conducted in the CCL using the size-classified samples of Illinois #6 coal and will be reported in future.

Table 2.8

**Elemental Ash Composition (Expressed as Oxides) in
the Illinois #6 Coal as Fired in the Multifuel Combustor**

Illinois #6 Coal Utility-grind Sample (ASTM Ash = 10.1 %)			
Oxide	Mass % of Coal	Oxide	Mass % of Coal
SiO ₂	4.64	CaO	0.53
Al ₂ O ₃	1.74	Na ₂ O	0.071
TiO ₂	0.092	K ₂ O	0.205
Fe ₂ O ₃	2.042	MgO	0.129

Table 2.9

**Elemental Ash Composition (Expressed as Oxides) in the Illinois #6 Coal
Used in Previous Experiments in the Char Combustion Laboratory**

Illinois #6 Coal (PSOC-1493d) 106-125 μm (ASTM Ash = 11.5 %)			
Oxide	Mass % of Coal	Oxide	Mass % of Coal
SiO ₂	4.23	CaO	0.458
Al ₂ O ₃	1.68	Na ₂ O	0.041
TiO ₂	0.092	K ₂ O	0.116
Fe ₂ O ₃	3.55	MgO	0.084

Figure 2.16 Comparison of the fractional release of iron as a fume from a raw coal (see Table 2.9) and a weathered sample of similar coal (see Table 2.8). Data for the raw coal are from the Char Combustion Laboratory. Data for the weathered coal are from the Multifuel Combustor.

Results from the MFC are consistent with those from the smaller-scale facilities. Coals that contain significant fractions of pyritic iron (typically pristine eastern coals) experience some iron loss during the early stages of combustion, whereas those with little or no pyritic iron (typically western and weathered eastern coals) experience none. These trends are illustrated in Fig. 2.17, where data from each of the coals are arranged again by rank. Confidence intervals (95%) are indicated for all data where finite amounts of iron are observed to be released from the coal. Those coals with no indicated confidence intervals had mean iron releases that were essentially zero. For several coals the mean iron releases are significantly different from zero, but the error bars on the data nonetheless include zero. For these coals, one cannot say with 95 % or more confidence that there was any iron release. In general, the relatively small number of samples on which the statistics are based is the underlying reason for the large confidence intervals. (One sample yields confidence intervals infinitely wide. Two samples yield 95 % confidence intervals ≈ 9 times larger than the standard deviation. Seven samples are required before the confidence intervals become smaller than the standard deviation.)

Figure 2.17 illustrates the trends seen in most of the MFC data. Coals with high initial pyritic iron fractions exhibit significant iron evolution during combustion. Coals with low initial pyritic iron concentrations exhibit little if any iron evolution. The initial pyritic iron concentration of the Mingo Logan coal was less than 50 %, which is uncommon for bituminous coals. It also exhibited no measureable iron release. The confidence intervals are compared in the figure to the magnitude of the release. Thus, the release of iron from the Upper Freeport coal is about 0.15 ± 0.05 , indicating with greater than 95% confidence that the release is greater than 0. The magnitude of the confidence intervals depends on both the consistency of the data and the number of data points available. The number of independently collected data points used to compute the results illustrated in the figure for the Pocahantas, Upper Freeport, Mingo Logan, and Pittsburgh coals, is eight, six, three, and three, respectively. This illustrates that the primary contributor to the size of the confidence interval is the number of points, with the consistency among the data being secondary. One independently measured data point in this context means that the raw coal is characterized, the coal is used in a MFC combustion test during which a fly ash sample is obtained, and the fly ash sample is analyzed. Overall mass loss is determined from tracer analysis, aluminium and titanium being the most commonly used tracers (Silicon loss is observed in the MFC tests, unlike the CCL and CDL tests. The difference in behavior in the facilities is presumed to be caused by the longer residence times in the MFC.)

Figure 2.17 MFC iron release results for four bituminous coals. The principal reason for the differences in confidence intervals is the number of independent samples available for analysis.

Similar data are available for each of the thirty coals tested in the MFC (see Table 2.2). The statistical analysis of these data is being completed now and the final results will be reported in the topical report soon to be completed on the release of iron during combustion. In general, only the pyrite-bearing coals exhibit iron loss during combustion, consistent with the data from the CCL and CDL.

Several observations from previously reported data can also be satisfactorily explained by the mechanism of iron release discussed in this paper. Raask reports studies [Raask, 1984; Raask, 1985] in which he observes the formation of an iron fume. In these studies, pure pyrite particles were rapidly heated in both oxidizing and reducing environments. Those introduced into an oxidizing environment produced an iron fume containing 0.1—0.5 μm particles. Raask attributed this to fragmentation of the pyrite particle during sulfur emission and subsequent decomposition to pyrrhotite.

Investigations of changes in mineral grain size distributions, including those of pyrite and its decomposition products, during the early stages of coal combustion have been reported on the same Illinois #6 coal used in our experiments [Baxter, 1990]. The results indicate that pyrite does fragment during decomposition, but the extent of fragmentation is insufficient to generate the fume. Furthermore, the mineral grain fragmentation which occurs during pyrite decomposition to pyrrhotite occurs a few milliseconds earlier than the fume formation illustrated in Figure 2.10. Fume formation is noted immediately after this decomposition by the mechanism described above.

Reported experimental data on size and composition of submicron particles formed during coal combustion compare favorably with these results [Flagan and Taylor, 1980; Taylor and Flagan, 1981; Taylor and Flagan, 1982]. In these studies, a subbituminous coal was combusted at both near-stoichiometric ($\phi = 0.96$) and fuel-lean conditions ($\phi = 0.57$). An enrichment of iron in the small particle sizes is observed at the near-stoichiometric condition and is much *more* prevalent at the fuel-lean conditions. In both cases, iron enrichment is more substantial than is silica enrichment in the small particle sizes. Specific data on the type of coal used and the forms of the mineral components in the raw coal are not given in the studies cited. Nevertheless, these results are consistent with the mechanism described above and would explain why iron was enriched in the small sizes as overall oxygen content increases. The data also indicate a peak in the iron particle size distribution of the fume at an aerodynamic diameter of 1 μm . If one assumes that these particles have specific gravities in the neighborhood of iron oxides (≈ 5), the actual particle diameters would be between 0.3 and 0.9 μm , consistent with the experimental results reported above, but much too large to be the consequence of a vaporization/recondensation process.

Conclusions

Experiments focused on the release of iron during coal combustion are reported. Experimental conditions of gas and particle temperature and gas composition were selected to represent those commonly found in pulverized-coal combustors during char oxidation. Carefully characterized, size- and gravity-classified coal particles containing iron in the form of pyrite were used in the experiments.

A rapid and extensive loss of iron from the coal particles during their early combustion history is observed. The iron loss is consistently observed immediately following coal devolatilization, during the incipient stages of heterogeneous char reaction. Approximately half of the iron in the coal is lost during this 25 ms period. This accounts for over 80 percent of the mineral lost from these coal particles in this experiment.

The data are not satisfactorily described by a reduction/vaporization process. The loss of iron is more rapid than can be explained by traditional models of vaporization rates. Furthermore, other, more volatile mineral components of the coal particles do not vaporize during these experiments.

A mechanism for the loss of iron is postulated based on these experimental data. The mechanism attributes the iron loss to the formation of an iron fume (particles $< 1 \mu\text{m}$) by chemical reaction of porous pyrrhotite grains with oxygen. These grains disintegrate when exposed to oxygen, releasing the iron fume. Part of the fume adheres to the char particle surface and the remainder is carried with the combustion products of char oxidation into the surrounding gas.

The mechanism is supported by all of the observations. Scanning electron micrographs reveal the porous pyrrhotite particles before the release of iron and the iron fume on the surface of the particles after the iron release. Disintegrated remains of pyrrhotite grains are also observed in the particles immediately after the loss of iron. The iron release is rapid and limited to the earliest stage of char combustion. No iron release is observed during the latter stages of char combustion. Transformations of pyrite to pyrrhotite occur before the release of iron, whereas transformations from pyrrhotite to oxides of iron occur as the fume is generated. Finally, the extent of iron loss increases as the penetration depth of oxygen in the particle increases, a trend opposite that predicted by vaporization mechanisms. Vaporization of iron-containing species does not satisfactorily explain these data.

Practical Implications

In a general sense, this investigation suggests that chemical reactions of mineral grains should be included as a source of mass in comprehensive descriptions of mineral release from coal or char particles. Iron fume is commonly observed in boiler fly ash at both pilot and commercial scale. The proportion of iron in the submicron particle size is too great to reasonably ascribe its formation to classical vaporization and recondensation processes. This investigation documents the formation of such material and its sensitivity: (a) to the form of iron in coal, (b) oxygen concentration, and coal weathering. We also postulate a formation mechanism consistent with all of our observations. While preoxidation will most likely decrease the amount of iron fume formation in existing and planned (e.s. Combustion 2000) coal utilization equipment, compared with the pristine, unoxidized samples discussed here, significant iron fume nevertheless will form under many conditions. This significant change in partitioning of iron throughout the fly ash size distribution will affect ash deposition rates, deposit properties, precipitator performance, and most other ash-related issues during pulverized coal combustion.

SUBTASK 2.2 THE EVOLUTION OF PARTICLE AND FLY ASH SIZE DISTRIBUTIONS

During this quarter, work continued to determine the extent of fragmentation and the resulting fly ash size distribution for several coals and coal blends. Coals examined range in rank from lignites to bituminous, and range in ash content from 5 to 22 %.

One of the unique aspects of these investigations is the use of the same *in situ* sizing technique to determine both char and fly ash particle sizes. Experiments are conducted in the Multifuel Combustor (MFC) using utility-grind, pulverized coal in an environment simulating that of a utility-scale boiler. Size distributions are measured immediately after coal devolatilization and at the end of char combustion (greater than 99% daf burnout as determined from tracer analysis of solid samples).

The extent of char fragmentation, as indicated by the number of fly ash particles formed per char particle, is found to depend on (in order of importance): (1) char structure, (2) initial char particle size, (3) ash content, and (4) mineral grain size distribution. The first three dependencies are clearly indicated by existing data. The fourth is postulated pending further investigation of mineral grain size distributions in these coal samples.

The analysis of the data collected from the MFC is similar to a previously published model of char fragmentation [Baxter, 1992]. This analysis is briefly reviewed here. The experimental design is also briefly reviewed. The bulk of the discussion centers on the results and their implications.

Theoretical Analysis

The fragmentation model described below relates the initial char (not coal) feedstock and final fly ash size distributions. The model is written in terms that are convenient for laboratory analyses. That is, the char particles have physical properties that can vary as a function of size but, at a given size, are described by a single-valued function. Particle-to-particle variations in physical properties *at a given size* are neglected. Also, transient developments in particle size distributions, as discussed by many of the previously cited authors, are neglected. Size distributions of the initial char and final fly ash can be related, in general, through a particle number balance.

$$\int_{d_{a1}}^{d_a} n'_a(x) dx = \int_{d_c=0}^{d_c=\infty} \int_{d_{a1}}^{d_a} g(x|y) dx n'_c(y) dy \quad (2.6)$$

The functions n'_a and n'_c represent particle concentration density functions for fly ash and char, respectively, with typical units of particles/(m³ μm). Dummy variables x and y are used in the integrands to represent fly ash (d_a) and char (d_c) particle diameters, respectively. Integration of n' with respect to particle diameter represents the cumulative concentration of particles with sizes between the limits of integration. Thus, the integral on the left represents the total concentration of fly ash particles with diameters larger than d_{a1} and smaller than d_a .

The function $g(x|y)$ is a conditional fly ash particle size distribution (psd); it indicates the *ultimate* size distribution of fly ash particles formed from a char particle with *initial* size y . This represents the only portion of the above equation that is not determined experimentally in this investigation.

Several published theoretical and experimental results suggest general forms of the function. One example [Quann and Sarofim, 1986] provides data from which $g(x|y)$ can be determined for one char particle size. In that study, coal particles were mechanically sieved to a 140 μm nominal diameter and combusted at a particle temperature of about 2000 K in a 20 % O_2 environment. The number of fly ash particles generated was deduced as a function of fly ash particle size.

The function $g(x|y)$ for this literature data [Quann and Sarofim, 1986] can be generated by differentiating the cumulative size distribution with respect to particle size. This is illustrated in Figure 2.18. The linearity of the data when plotted in this way suggests that the data follow a power-law distribution, i.e.,

$$g(x|y) = \begin{cases} a(y)x^b, & \text{for } x_1(y) \leq x \leq x_2(y), \\ 0 & \text{otherwise} \end{cases} \quad (2.7)$$

where x_1 and x_2 represent the diameters of the smallest and largest fly ash particle generated, respectively. This conditional psd describes a power-law size distribution between the limits x_1 and x_2 for fly ash particles generated from each char particle of size y . Note that this functional form can only describe the results from an ensemble of initial char particles with size y . The functional form of g for a single char particle is series of Dirac delta functions.

Values for a and b of 3260 and -3.21, respectively, fit the literature data [Quann and Sarofim, 1986] with a coefficient of determination [Canavos, 1984] (r^2) greater than 0.99 (in logarithmic coordinates with x expressed in microns). The original data of Quann and Sarofim have been recast in number density form, and this correlation is compared with these recast data in Figure 2.18. The authors state that the smallest particles (those smaller than about 0.6 μm) are generated by vaporization-recondensation mechanisms, whereas the larger particles are believed to be generated by surface drop shedding or disintegration of char structures. If the data at sizes smaller than 0.6 μm are eliminated, values for a and b of 2370 and -2.95, respectively, fit the remaining data, also with a coefficient of determination greater than 0.99. Therefore, the functional form for $g(x|y)$ given by Eq. 2.7 represents at least this set of data regardless of the mechanism of fragmentation and the value of b used in the conditional psd can be assumed to be approximately -3.

Results of a percolation model of char fragmentation [Dunn-Rankin and Kerstein, 1988] provide further theoretical motivation for this functional form of this conditional pdf. This formulation has been used in other theoretical studies of the transient evolution of char particle size distributions [Kerstein and Edwards, 1987].

Figure 2.18 Power law function $g(x|y)$ correlated with the power-law size distribution. Data are from the literature [Quann and Sarofim, 1986].

A mass balance on the fly ash determines the function $a(y)$, as follows:

$$m_a(y) = \int_0^{\infty} \frac{\pi}{6} \rho_a x^3 g(x|y) dx = \frac{\pi}{6} \rho_a a(y) \Delta x(y) = \omega_a(y) m_c = \omega_a(y) \frac{\pi}{6} \rho_c y^3 \quad (2.8)$$

where ρ represents density, ω represents ash mass fraction, and Δx represents $x_2 - x_1$. Note that the density of the *initial* char particle (ρ_c) represents the density of the total particle, not just the organic portion. Also, the density of the *final* ash particle and the ash mass fraction in the char particle (ρ_a and ω_a , respectively) represent values of *ash*, as opposed to the mineral matter from which the ash is formed. It follows from Eq. 2.8 that,

$$a(y) = \frac{\omega_a(y) \rho_c y^3}{\rho_a \Delta x(y)} \quad (2.9)$$

For convenience in determining the upper and lower bounds of g , a parametric function $f(y)$ is designated the *fragmentation factor* and is defined as follows:

$$f(y) \equiv \frac{(\omega_a \rho_c / \rho_a)^{1/3} y}{x_2} \quad (2.10)$$

The numerator represents the size of the fly ash particle that obtains when all of the ash in a char particle coalesces, i.e., no fragmentation occurs. The function f equals the ratio of this hypothetical size to the size of the largest fragment actually generated from a char particle (x_2); f increases with an increase in the *extent* of fragmentation. In the limit of no fragmentation, f is unity, independent of either initial char particle size (y) or char size dependencies in either ρ or ω . (This statement may appear to contradict the explicit dependence of f on y indicated in Eq. 2.10. However, in the case of no fragmentation, this explicit dependence cancels with the implied dependence of x_2 and of the physical properties on y .) In general, f is expected to be greater than or equal to 1. The parameter f indicates the extent of fragmentation in that it increases as the extent of fragmentation increases. If char were to produce a monodispersion of fly ash particles as a consequence of fragmentation, the total number of fragments produced would be equal to f^3 .

A second function $s(y)$, designated the *fragment size ratio*, is defined as

$$s(y) \equiv \frac{x_1(y)}{x_2(y)} \quad (2.11)$$

and represents the *mode* of fragmentation in the sense that s decreases as the range of fragment sizes produced from a char particle increases. If there is no fragmentation, both f and s are unity. As s decreases from unity toward zero, the range of sizes of fragments produced from a single char particle increases.

Equation 2.7 can be written in terms of the parameters f and s as

$$g(x|y) = \begin{cases} \frac{\omega_a \rho_c y^3}{\rho_c \Delta x} x^{-3} & \text{for } x_1(y) \leq x \leq x_2(y) \\ 0 & \text{otherwise} \end{cases} \quad (2.12)$$

yielding

$$\int_{d_{a1}}^{d_a} g(x|y) dx = \frac{f^3}{2} \left(\frac{1-s^2}{s^2-s^3} \right) + \min \left\{ \frac{f^3}{2(1-s)} \left[\left(\frac{x_2}{\min(x_2, d_{a1})} \right)^2 - \left(\frac{1}{s} \right)^2 \right], 0 \right\} + \min \left\{ \frac{f^3}{2(1-s)} \left[1 - \left(\frac{x_2}{\max(x_1, d_a)} \right)^2 \right], 0 \right\} \quad (2.13)$$

where s , f and x_2 depend on y . The second term on the right side is negative for all y where $d_{a1} > x_1$ and the third term is negative for $d_a < x_2$. Otherwise, both terms are zero. If all particle sizes are included in the integration ($d_{a1} = 0$ and d_a larger than the largest char or fly ash particle in the stream), the only nonzero term on the right side of the equation is the first term, which represents the ratio of the total numbers of fly ash and char particles.

In general, both f and s depend on initial char particle size y . However, the qualitative relationship between initial char and fly ash particle size distributions is conveniently illustrated by assuming that f , s and the ratio $(\omega_a \rho_c)/\rho_a$ are independent of initial char particle size and can be treated with average values. This means the char particles are homogeneous, or size-invariant, with respect to both their physical properties and their fragmentation properties and that the behavior of particles in a given size range can be represented by statistical averages of properties. Under these assumptions,

$$x_2 = \left(\frac{\omega_a \rho_c}{\rho_a} \right)^{1/3} \frac{y}{f} \equiv py \quad (2.14)$$

and

$$x_1 = sx_2 = psy \quad (2.15)$$

where p is independent of y and typically has a value of order 0.5 or less. This allows the integral of the conditional psd to be expressed analytically in terms of y only. If all ash particles are included in the integration ($d_{a1} = 0$), the relationship between char and fly ash concentration distributions can be written as

$$\int_0^{d_a} n'_a(x) dx = \int_0^{d_a/(ps)} n'_c(y) \frac{f^3}{2} \left(\frac{1-s^2}{s^2-s^3} \right) dy + \int_{d_a/p}^{d_a/(ps)} n'_c(y) \frac{f^3}{2(1-s)} \left[1 - \left(\frac{py}{d^a} \right)^2 \right] dy + \quad (2.16)$$

A linear transformation of this equation relates directly to the experimentally measured cumulative particle size distributions reported later. This transformed expression is

$$K_a(d) \equiv \int_d^\infty n'_a(x) dx = \int_0^\infty n'_a(x) dx - \int_0^d n'_a(x) dx \quad (2.17)$$

where the integral from 0 to ∞ is a constant (independent of d_a). A similar expression defines the function K_c for the char particles.

$$K_c(d) \equiv \int_d^{\infty} n'_c(x) dx = \int_0^{\infty} n'_c(x) dx - \int_0^d n'_c(x) dx \quad (2.18)$$

These cumulative distributions will be used in the discussion of the experiments that follows.

Dependence of the fly ash psd on the extent of fragmentation (f) under these assumptions is straightforward; the ratio n'_a / f^3 is independent of f when plotted as a function of the dimensionless size pd_a . Dependence on mode of fragmentation (s) is more complex. This is discussed in more detail elsewhere [Baxter, 1992].

Limiting forms of Eq. 2.6, other than Eq. 2.16, are useful to consider. If the initial char particles are monodisperse (n'_c is a Dirac delta function), the integral on the left represents the total number of fly ash particles produced per char particle. Assuming Eq. 2.7 as the appropriate description for g , the total number of fly ash particles generated per char particle becomes

$$g = \frac{f^3}{2} \left(\frac{1+s}{s^2} \right) \quad (2.19)$$

Eq. 2.19 indicates the dependence of the number of fly ash particles on the parameters f and s . For a given value of f , the number of fly ash particles increases dramatically as s decreases (recall that s is always less than or equal to 1). Similarly, as f increases for a given value of s , the total number of fly ash particles increases as f^3 .

The valid range of the functions f and s illustrate that this theoretical approach is applicable only to ensembles of particles, not to individual particles. For example, when the ash in an individual particle coalesces to form a single fly ash particle ($f = 1$), there is only one size fly ash particle produced ($s = 1$). However, only a fraction of the particles in an ensemble of nominally identical char particles may behave this way. Therefore, f can assume a value of unity for the ensemble without limiting the range of values s can assume. In the application of this theory in this work, the only theoretical limitations on these two parameters are that $f \geq 1$ and $s \leq 1$. The functions are independent of each other.

Experimental Conditions

The Multifuel Combustor (MFC) and a Particle Counter Sizer Velocimeter (PCSV) are the primary experimental facility and diagnostic, respectively, used in this work. The MFC provides careful control of gas temperature and composition in a long-residence-time facility. The MFC was operated at a firing rate of 0.07 MBtu/hr with overall oxygen concentrations varying from 5 to 3 mole % during char oxidation, conditions similar to commercial-scale boiler operation. Particle residence time is varied by moving the location of the coal injection lance to various ports along the length of the combustor.

The PCSV performs *in situ* measurements of particle frequency (count), size and speed at the base of the combustor. The PCSV is based on near-forward light scattering from laser beams focused at the center of the reactor flow. Two laser beams are used, one for large particles ($> 3 \mu\text{m}$) and the second for small particles. The measurements are based on individual particles passing through an approximately ellipsoidal diagnostic volume with a major axis of about 1 mm and minor axes of approximately $300 \mu\text{m}$ for one beam and $50 \mu\text{m}$ for the second. The diagnostic is discussed more fully in the literature [Holve and Self, 1979a; Holve and Self, 1979b; Holve, et al., 1981].

We determined the accuracy of the instrument by passing monosized standards through the diagnostic volume and comparing the measured particle sizes with the known actual sizes. Standards used included glass beads entrained in air and transparent discs etched in an opaque reticule. The standards varied from 0.6 to $60 \mu\text{m}$ and indicate that the PCSV reports particle sizes within one size bin or $0.1 \mu\text{m}$ of the correct size, whichever is larger.

The precision of the data is determined by repeating measurements of coal and fly ash in the MFC under nominally identical conditions and computing coefficients of variation from the results. At least five, and as many as twelve, replicate experiments were performed for each coal at each sampling height. The coefficient of variation thus determined includes experimental uncertainty as well as actual fluctuations due, for example, to turbulent fluctuations and variations in coal feed rates. The impact of such fluctuations on the data can be minimized by computing the total mass flowrate from the measured particle concentrations and normalizing all the results to this value. Confidence intervals presented below are based on these measured coefficients of variation and standard statistical techniques.

The upper and lower detection limits of the PCSV are determined in these experiments by the points at which the agreement among the repeated tests becomes poor, as indicated by the statistical confidence intervals. The lower limit is $0.4 - 0.7 \mu\text{m}$ and is controlled primarily by signal-to-noise levels in the detector. The upper limit is controlled by sampling statistics in this experiment. Approximately 160,000 individual particles were sampled per measurement, and each measurement was repeated 5 to 12 times. Under these conditions, the upper detection limit is about $100 \mu\text{m}$.

Reasonably complete analyses of all the coals used in these experiments are included in the appendix. The data in the appendix include all of the coals used in the program to date. There are several samples of coal with the same name. These are distinguished by numbers, for example, Illinois #6 (2) is a different coal sample than Illinois #6 (1).

The nominal conditions under which these experiments were conducted are summarized in Table 2.10. Under these experimental conditions, the particles form a dilute phase in the gas, with the total particle volume fraction far less than one percent of the overall gas volume. Consequentially, the probability of particle-particle collisions producing agglomerated fly ash is vanishingly small.

Table 2.10

Typical Local Gas and Particle Properties in the MFC at the Initial Char and the Fly Ash Measurement Locations

<u>Property</u>	<u>Initial Char</u>	<u>Fly Ash</u>
Gas temperature (°C)	1100	900
Oxygen mole fraction	0.06	0.04
Particle residence time τ (s)	0.2	2.1
Particle burnout (daf)	0.65	0.99+
Particle temperature (°C)	1250	900

Coals and Coal Properties Studied

Analyses of all of the raw coals used in this study were completed this quarter. These analyses were performed as a contribution in support of this research by CONSOL Inc. These analyses include: (1) moisture content; (2) proximate analysis; (3) ultimate analysis; (4) ash chemistry; (5) ash fusion temperatures under reducing and oxidizing environments; (6) sulfur forms; (7) particle size distributions determined by sieves; (8) particle size distributions determined by Malvern optical analyses, (9) chlorine content (for coals containing appreciable chlorine), and (10) heating value. In all cases, the data are averages of several replicated measurements. The statistical analysis of the data is complete but is not presented here. The statistical certainty with which the chemical and physical properties of the raw coal are known are used in determining error bars for experiments and, in the future, will be used for predictions. A complete specification of each coal will be included in the appendix of the final report to be submitted to PETC shortly.

The range of coals and coal properties covers the range of commercially significant steam coals rather thoroughly. Coals from essentially every major coal producing region of the US are represented. Coals range in rank from lv bituminous to lignite.

We have obtained fragmentation data for all of the coals. There is a great deal of similarity and consistency among the data for similar coals. Rather than present all of the data, much of which is repetitious, we have collected data for representative coals of every major rank and field. In the discussion below, we focus upon the important trends observed in these collections of data.

Experimental Results and Discussion

Data derived from many coals are presented below. The discussion will first contrast a typical swelling coal (Pittsburgh #8) and a non-swelling coal (Roland coal). Results from the remainder of the coals will be presented in the context of the results from these two coals and will be shown to be consistent in their interpretation.

Cumulative size distributions for char and fly ash particles generated from the Pittsburgh #8 (2) coal are illustrated in of Fig. 2.19a. The mean value of the several measured distributions is indicated together with 95% confidence intervals. The coefficients of variation (standard deviation divided by mean) used in computing the confidence intervals are illustrated as a function of particle size in Fig. 2.19b. These experimentally determined coefficients of variation are largest at small particle sizes. Light scattering intensity is lowest for small particles and is most influenced by experimental error (detector noise, beam steering, etc.), giving rise to higher coefficients of variation.

The data illustrated in Fig. 2.19 are representative of all of the coals studied. Only the final results of the fragmentation analysis will be presented for the remainder of the coals studied.

The confidence intervals are largest for the submicron-sized char particles. These, however, are of little consequence to the analysis since they form fly ash particles too small to reliably detect with this technique. Over the range of char and fly ash particle sizes of interest in this study, the size distributions are determined within approximately ± 20 relative percent accuracy. The confidence intervals are much smaller over most of the range of interest.

Using these data, the fragmentation factor f is computed according to the equations indicated in the preceding discussion. The only quantity not determined from the measurements is s . Figure 2.20a illustrates the computed value of f for an assumed value of s of unity. This is equivalent to assuming that equal-sized fly ash particles form from a char particle of a given initial size. While this assumption is probably not realistic, it is convenient for engineering models (such as ADLVIC) that incorporate fragmentation behavior.

As illustrated in Fig. 2.20a, the value of the fragmentation factor exceeds unity only for initial char particle sizes larger than about 20 μm . The size of fragments generated by the fragmentation of these large particles is indicated by the second abscissa at the top of the figure. Fly ash particles generated through fragmentation are concentrated in the 10 μm size range.

The fragmentation factor should range from 1 to larger values, as can be seen from its definition (Eq. 2.10). The experimental measurements indicate a fragmentation factor as low as 0.7 in some regions of char and fly ash sizes. This is probably associated with variations in the char density and ash mass fraction and the fly ash density as a function of particle size. Reliable information concerning the particle size variation of these physical properties is not available for this coal. Therefore, the properties were assumed to be equal to their average values at all particle sizes. Considering that the fragmentation factor is derived entirely from experimental data, this small deviation of the experimental value below its theoretical limit is viewed as only a minor concern in these results.

Results from similar measurements and analyses for a Roland-seam coal are illustrated in Fig. 2.21. The ordinates of the two panels in Fig. 2.21 are scaled the same as those in Fig. 2.20 to allow a direct comparison. The lower-rank Roland coal is seen to fragment less extensively than the Pittsburgh #8 bituminous coal. This is consistent with our previous results and with the postulate that fragmentation is strongly influenced by char structure [Baxter, 1992]. Coals that form chars that are cenospheres or 'mesospheres' (have very large voids) are more likely to

Figure 2.19 Cumulative particle size distributions and statistics for char and fly ash generated from the Pittsburgh #8 (2) hv A bituminous coal.

Figure 2.20 Variation of the fragmentation factor with initial char particle size and fly ash size (a) and the number of fly ash particles formed per char particle as a function of initial char particle size (b) for the Pittsburgh #8 hv A bituminous coal.

Figure 2.21 Variation of the fragmentation factor as a function of initial char and final fly ash particles sizes (a) and of the number of fly ash particles produced per char particle as a function of initial char particle size (b) for a Roland-seam subbituminous coal.

fragment because they have inherently unstable structures as they burn out. Such is the case with high volatile bituminous coals. Chars that do not form cenospheres, such as the Roland coal, are stable as the char particles burn out. The fragmentation data reflect the stability of the char structure in that there are few fragments formed per original char particle.

The comparison of the Pittsburgh #8 and Roland coals is representative of all of the coals we have tested. Data for additional coals and coal blends are illustrated in Figures 2.22 through 2.26. These data are consistent with earlier observations, i.e., the extent of fragmentation generally increases with increasing char particle size, is greater for chars that form cenospheres than for more dense chars, and decreases with increasing ash loading. While these general characteristics are consistent among all of the data, some details of the data that need further explanation.

Data for the Utah Blind Canyon coal, which is borderline between hv A and hv B bituminous, indicate little fragmentation at any particle size, much the same as the Roland and other subbituminous coals and lignites examined. When compared to the other bituminous coals, the behavior of the Blind Canyon coal appears anomalous. This is only an apparent anomaly, as can be verified by a more detailed investigation of the chemistry of the Utah Blind Canyon coal.

Figure 2.27 indicates the detailed chemical structure of coals from many of the same seams used in this experiments, including the Blind Canyon coal. These data are taken from published NMR spectroscopy results [Solum, et al., 1989], for coals obtained from the Argonne premium coal bank, not the samples of the coals tested here. The Blind Canyon coal in the Argonne coal bank is chemically more similar to the lower-rank subbituminous coals and lignite than it is to even to the hv B bituminous samples. There are no samples of hv C available for comparison with these data. We postulate this chemical difference is the reason for the different fragmentation behavior. Coal rank is based solely on heating value and moisture content for these coals (as determined by ASTM D388-36) and is only a crude indicator of the actual chemical structure of the raw coal.

The influence of ash loading on fragmentation behavior is minor. This can be seen by comparing results for the Kentucky #9 coal with the Illinois #6 (1) coal shown in Fig. 2.28 and Fig. 2.29. With reference to Table 2.2, these two coals are seen to be similar in most respects, with the exception that the Kentucky #9 coal has roughly 50% higher ash content than the Illinois #6 (1) coal. Comparison of the similar data for the Kentucky #9 and Illinois #6 (1) coals with the data for the Beulah lignite (Figs. 2.28 and 2.29) clearly underscores the dominant importance of coal rank on fragmentation behavior.

Conclusions

The fragmentation data investigated thus far show consistent trends in that: (1) large char particles produce far more fly ash particles than small char particles; (2) the extent of fragmentation tends to increase with increasing coal rank through hv bituminous; (3) the extent of fragmentation tends to decrease with increasing ash loading; and (4) in all cases studied thus far, the total increase in the number of particles greater than 0.6 μm in diameter by char fragmentation is less than a factor of two.

Figure 2.22 Variation of the fragmentation factor as a function of initial char and final fly ash particle sizes (a) and of the number of fly ash particles produced per char particle as a function of initial char particle size (b) for a Kentucky #11 hv B bituminous coal.

Figure 2.23 Variation of the fragmentation factor as a function of initial char and final fly ash particle sizes (a) and of the number of fly ash particles produced per char particle as a function of initial char particle size (b) for a Utah Blind Canyon hv A bituminous coal.

Figure 2.24 Variation of the fragmentation factor as a function of initial char and final fly ash particle sizes (a) and of the number of fly ash particles produced per char particle as a function of initial char particle size (b) for the Illinois #6 (2) hv B bituminous coal.

Figure 2.25 Variation of the fragmentation factor as a function of initial char and final fly ash particle sizes (a) and of the number of fly ash particles produced per char particle as a function of initial char particle size (b) for a Decker subbituminous A coal.

Figure 2.26 Variation of the fragmentation factor as a function of initial char and final fly ash particle sizes (a) and of the number of fly ash particles produced per char particle as a function of initial char particle size (b) for a blend of 70 % Roland and 30 % Illinois # 6 (2) coals.

Figure 2.27 Comparison of the chemical composition of Argonne coal bank samples [Solum, et al., 1989] contrasting the Blind Canyon coal with coals similar to several used in these experiments.

These general trends have been established for a significant number of coals over a broad range of rank, ash loading, and particle size. Our results indicate substantial agreement among experimental results previously thought to be in disagreement.

In particular, the dependence of char fragmentation on char particle size had not previously been recognized when comparing results from different systems. The implications of this particle-size dependence reconcile, in part, seemingly discrepant results previously reported in the literature. This is discussed in more detail elsewhere [Baxter, 1992]. Furthermore, the current study clearly indicates that, for typical coals in typical combustion environments, the extent of fragmentation experienced at all char particle sizes is relatively minor.

Finally, based upon our extensive data sets for a broad range of coals, a mechanistic description has been developed that predicts the trends observed in the data. However, significant additional work needs to be performed to establish quantitative relationships between fly ash chemistry and the size distributions of both the char particles and the mineral grains within the char particles.

Figure 2.28 Variation of the fragmentation factor as a function of fly ash particle size for the Illinois #6 (1) hv C bituminous coal, the Kentucky #9 hv C bituminous coal, and the Beulah lignite.

Figure 2.29 Variation of the number of fly ash particles produced per char particle as a function of initial char particle size for the Illinois #6 (1) hv C bituminous coal, the Kentucky #9 hv C bituminous coal, and the Beulah lignite.

Practical Implications

Although it is not included in this report, our data on coal (as opposed to char) fragmentation indicate that no fragmentation occurs during the early stages of coal combustion. These data will be presented in the final report under preparation. Combination of the coal and char data indicate that fragmentation under typical pulverized-coal-fired conditions of particle size and oxygen concentrations: (1) is most significant for cenosphere-forming coals, (2) decreases slightly with increased ash loading, and (3) is not a first-order effect.

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 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, among of the more significant reactions with respect to deposit formation, occur 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.

Development of an optical, *in situ*, real-time technique, when combined with the MFC and deposition probes, will provide a unique capability to explore the chemical species transformations that occur in an ash deposit during combustion.

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, the utility of the technique is clearly demonstrated. More refined analyses of data will be presented, in the future, after we install a mirror-based optical system and upgrade the computational resources of the FTIR.

Fuels, Equipment, and Experimental Design

Fuels

Chemical and combustion analyses of the coals used in this investigation are indicated in Table 2.11. Spectra from the Antelope and Black Thunder coals are discussed later. Both are typical Powder River Basin (PRB) coals. 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 values indicated are derived from analyses of the Sandia samples of the coals and may differ somewhat from analyses from other samples. The coals are quite similar in both organic and inorganic composition, although they differ significantly in chemical composition of the deposits they form.

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

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 820 K. Finally, we incorporated some new features in the probes, such as an in-line heater, to provide greater flexibility in controlling probe surface temperature. The design features of the probe are discussed below.

The FTIR spectra presented 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.

Table 2.11 Chemical and combustion properties of the fuels and the blend used in the combustion tests.

	<i>Black Thunder</i>	<i>Antelope</i>
H ₂ O (mass %)	21.30	22.90
Ash (mass %, dry)	6.46	5.51
Ultimate Analysis (mass %, dry basis)		
C	69.90	68.38
H	5.05	4.89
O	17.09	19.74
N	0.94	1.03
S	0.48	0.42
Cl	0.08	0.03
Proximate Analysis (mass %, dry basis)		
Fixed Carbon	39.28	51.22
Volatile Matter	54.26	43.27
Ash Chemistry (% of Ash)		
SiO ₂	30.31	25.03
Al ₂ O ₃	16.27	11.36
TiO ₂	1.27	0.66
Fe ₂ O ₃	5.04	8.18
CaO	21.07	28.88
MgO	4.74	5.60
K ₂ O	0.35	0.25
Na ₂ O	1.41	1.57
SO ₃	17.46	17.65
P ₂ O ₅	0.91	0.81
undetr. Ash	1.17	0.01
Total	100	100
Forms of Sulfur (mass % of dry fuel)		
Sulfatic	0.00	0.00
Pyritic	0.08	0.02
Organic	0.40	0.40
HHV (dry basis) [Btu/lb]	12815	12271

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. 2.30). 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 instrumented with thermocouples 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 FTIR spectra collected under these conditions can be used to determine surface composition, temperature, and possibly deposit thickness.

Figure 2.30 Schematic diagram of a deposition probe used in the MFC experiments. Note that nominally uniform deposits are grown on all sides of the probe by rotating it in the flow, allowing FTIR spectra to be collected from the bottom shadowed surface.

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 FTIR spectra to be collected from one location on the probe at successive

times, thus 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.

An in-line air heater (maximum heater temperature ≈ 1300 K) is used to control probe surface temperature over a broader range than is achievable by room temperature air alone. Probe surface temperatures vary from 500 K to 950 K, consistent with variations typical for heat transfer surfaces in 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.

Optics

Two optical systems have been used to collect radiation from the deposition probe. They are both discussed below. Only modest changes to these systems have been made in the last quarter. Most of the data presented here were, in fact, collected with the original optical system. During the last quarter, these data have been reanalyzed with new algorithms to determine the extent to which the original interpretations may have been influenced by gas-phase interference in the spectra.

The original optical system is shown in plan view in Fig. 2.31. 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 (254 mm focal length) is protected from the gases and from particles in the combustion flow by an air purge incorporated around its mount. Between measurements it is protected by physical barriers. 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 optical properties of the deposit material. It varies from several multiples of the wavelength of the radiation, in weakly absorbing regions of the infrared spectra, 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.

Figure 2.31 Optical layout of the FTIR experiment for measuring deposit species composition on tubes in cross flow.

Improved optical performance (stronger signal, same noise) has been achieved in our new, improved system using 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 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 380 mm, 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 interferometer were 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 add noise and can overwhelm the controller and A/D converters of the instrument. This problem is eliminated 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.

Other changes to the system include installation and use of an off-axis parabolic "flipper" mirror. The conceptual function of the mirror is illustrated in Fig. 2.31. 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.

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 combustion gas temperatures used (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 precludes getting clear indications of whether some peaks originate in the gas or from the surface. We find an optimal resolution to be $2\text{-}4\text{ cm}^{-1}$ 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)

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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

$$S(\bar{\nu}, T) = I(\bar{\nu}) [\epsilon_s(\bar{\nu}, T_s) P(\bar{\nu}, T_s) + G(\bar{\nu}, T) + O(\bar{\nu}, T)] + B(\bar{\nu}, T_i) + N(\bar{\nu}) \quad (2.20)$$

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.

Identification of chemical species 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. 2.20, and each of the terms in the equation is discussed in more detail below in pursuit of this objective.

The Planck function, P , is given by

$$P(\bar{\nu}, T) = \frac{2hc^2\bar{\nu}^3}{\exp(hc\bar{\nu}/kT) - 1} \quad (2.21)$$

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.

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. As shown in Fig. 2.32 the measurements indicate that the instrument

response function varies by less than 3 % over the region 450 to 4000 cm^{-1} . 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. 2.33 and was not allowed to vary with temperature in performing the calculations shown in Fig. 2.32. 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 are negligible in Eq. 2.20. 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. 2.20, again assuming that all terms other than the background and noise terms are 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).

Figure 2.32 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.

Extraneous radiation from other sources (the term represented by O in Eq. 2.20) 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 (≈ 60 K).

Figure 2.33 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.

Gas-phase emission peaks cannot be ignored in the data analysis. Over some regions of the infrared spectrum, the gases are transparent and contribute nothing to the signal. However, in regions where the gases are optically active, they emit very strongly and are commonly optically thick. In this case, they completely obscure surface emission of the same frequency. They can also have the effect of introducing false features or distorting true features in the resulting spectra [Baxter and Hardesty, 1993c]. 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].

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. 2.34 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 structure. This suggests that emissivities measured by this experimental technique are accurate to well within 5 percent.

Figure 2.34 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 fine structure in the results above 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. Below 450 cm^{-1} the detector has essentially no sensitivity. The results illustrated in Fig. 2.34 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. 2.20 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. 2.20 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.

In the first method, 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 determined by

$$\Delta S = S_2 - S_1 = I(\bar{\nu}) \left[\epsilon_{s,2}(\bar{\nu}, T_{s,2}) P_2(\bar{\nu}, T_{s,2}) - \epsilon_{s,1}(\bar{\nu}, T_{s,1}) P_1(\bar{\nu}, T_{s,1}) \right] \quad (2.22)$$

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 this method 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 (± 40 K) temperature variations between the two signals are of little consequence to the result. The primary advantages of the technique are: (1) accurate elimination of background contributions (O and B) and (2) ease of analysis.

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

$$\epsilon_2(\bar{\nu}, T_2) = \frac{S_2(\bar{\nu}, T_2)}{S_1(\bar{\nu}, T_1)} \epsilon_1(\bar{\nu}, T_1) \quad (2.23)$$

This method assumes that the dominant term in Eq. 2.20 is the emission from the surface (rather than emission from the gases or from background sources). 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, 1993a; Baxter and Hardesty, 1993b; Baxter, et al., 1993c]. In the future, more extensive use will be made of the instrument response function in analyzing the data. There have also been improvements in other aspects of the data analysis.

Results

To date spectra have been collected from both metallic and ceramic heat exchange surfaces with surface temperatures varying from 500 to 900 K. Deposits have been generated from a suite of coals and from 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 in previous quarterly reports [Baxter and Hardesty, 1993a; Baxter and Hardesty, 1993b; Baxter and Hardesty, 1993c].

This quarter, we collected for the first time quantitative results on the surface emissivity of deposits as a function of wave number. Complete statistical analyses of these results are not yet complete. However, data from the blackbody are accurate to within $\pm 1.5\%$ (see Fig. 2.34). Our current estimate of the uncertainty of the data from the probe is $\pm 10\%$, with the dominant portion of the uncertainty in emissivity arising from uncertainty in the deposit surface temperature.

The Antelope and Black Thunder coals are used to illustrate two types of information obtained recently in Figures 2.35 and 2.36. Spectral emissivities of deposits over the range 3500 to 500 cm^{-1} ($2.9\text{ }\mu$ to $20\text{ }\mu$) are illustrated as a function of growth time. In the region from 1400 cm^{-1} to 500 cm^{-1} , these data can be used to identify chemical species in the deposits. The changing deposit composition with time, and the differences in deposit composition between these two otherwise similar coals, are also illustrated by the data in the figures.

Figure 2.35 illustrates the time development of the spectral emissivity of a deposit generated from the Antelope coal for the first three hours of deposition. The probe used in these experiments was a polished, stainless steel tube. Both the first and last results are shown as solid lines, with the first being the largely featureless spectrum at the bottom of the family of spectra and the last result (180 min) being the spectrum at the top of the family of spectra. The large feature located from 2200 to 2400 cm^{-1} is the effect of CO_2 emission, as is the narrow feature at about 670 cm^{-1} . The remaining features are attributable to chemical species accumulating on the surface, and several changes can be noted as time develops. For example, the feature becoming increasingly prominent in time at about 950 cm^{-1} is believed to be indicative of the formation of silicate material (analysis is continuing).

The emissivity is shown at unevenly spaced time increments. In particular, the time between the last two results is larger than the total time associated with the first four results. The relatively minor changes in emissivity between these two times indicates that the deposit has become essentially opaque and, were it not for changes in the deposit chemistry, would assume a spectral emissivity that does not change in time.

The deposit emissivity is influenced by both the structural properties of the deposit and the deposit chemistry. Collections of small, nonabsorbing particles form reflective surfaces, and for this reason the emissivity over much of the spectral region is low. It is fortuitous that it appears to be about equivalent to the emissivity of the polished probe. The Antelope coal used in these studies is from the Powder River Basin and these data illustrate experimental confirmation of the “reflective ash” characteristics associated with industrial use of these fuels.

Figure 2.35 Spectral emissivity of a deposit generated from the Antelope coal as a function of time during the first three hours of deposition.

Figure 2.36 illustrates similar spectral emissivity data for deposits generated from the Black Thunder coal. The dynamic development of the emissivity is qualitatively similar in both cases. Both coals produce deposits with relatively low emissivities (0.2 - 0.4 in most spectral regions). However detailed examination of the region between 1400 and 500 cm^{-1} reveals marked differences in deposit composition. The deposits from the Antelope coal are seen to contain more silica and less alumino-silicate than those from the Black Thunder Coal. Silica is indicated by the feature at about 1100 cm^{-1} , whereas silicates are indicated by features from 900 - 1050 cm^{-1} . Spectra from both deposits illustrate the dynamic formation of sulfates, indicated by features at 1150 - 1120 cm^{-1} .

It is interesting and relevant to note that utility experience with these two coals, in both pulverized-coal and cyclone-fired boilers, suggests that they produce ash deposits having considerably

different properties, despite the similarity in the coal ash analyses [Brobjorg, 1993]. Our results illustrate how the new surface diagnostic can identify these differences *in-situ* and in real time. Further analysis of these and other spectra will continue over the next quarter.

Figure 2.36 Spectral emissivity of an ash deposit generated from the Black Thunder Coal during the the first 2.5 hours of deposition.

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PLANS FOR NEXT QUARTER

The research reports on iron release during combustion, release of inorganic material during combustion, and coal fragmentation will be finalized in the next quarter. Also, work on spectral emissivities will continue. Interactions with PETC researchers (Everett Ramer) were initiated late in this quarter and will continue of the next several quarters.

ACKNOWLEDGMENTS

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) played a leading role in performing the FTIR measurements in the combustor. Gian Sclipa and Al Salmi were also instrumental in operating and maintaining the combustor this quarter and in assisting in the 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 completed in the last quarter.

Baxter, L.L., G.H. Richards, D. K. Ottesen, and J. N. Harb, "*In situ*, Real-Time Characterization of Coal Ash Deposits in a Pilot-Scale Combustor Using Fourier Transform Infrared Emission Spectroscopy," accepted for *Energy & Fuels*.

Baxter, L.L., "Development of Emission FTIR Spectroscopy as a Diagnostic for Ash Deposition During Coal Combustion" 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," presented at the Ninth Annual Coal Preparation, Utilization, and Environmental Control Contractors Conference, Pittsburgh, PA, July 19-22, 1993.

Baxter, L.L., "Ash Deposition during Combustion of Powder River Basin Coals," invited presentation at the Wester Fuels Conference, Kansas City, MO, August 22-24, 1993.

Abbott, M.F., R.E. Douglas, C.E. Fink, N.J. Deluliis, and L.L. Baxter, "A Modeling Strategy for Correlating Coal Quality to Power Plant Performance and Power Costs," presented at the Engineering Foundation Conference on Ash Deposition in Boilers, Solihull, UK, June 21-25, 1993.

Baxter, L.L., and P. J. Smith, "Turbulent Transport of Particles," accepted for *Energy & Fuels*, 1993

Wall, T., and L. L. Baxter, "Fouling and Slagging Associated with Coal Blending and Switching: Implications for Thermal Performance," the Engineering Foundation Conference on Coal Blending and Switching of Western Low-Sulfur Coals, Snowbird, UT, September 26 - October 1, 1993

L. L. Baxter, "Experimental and Theoretical Comparison of the Combustion and Ash Deposition Behavior of Blended Coals and that of the Blend Components," the Engineering Foundation Conference on Coal Blending and Switching of Western Low-Sulfur Coals, Snowbird, UT, September 26 - October 1, 1993

Baxter L.L., "The Fate of Mineral Matter During Pulverized Coal Combustion," presented at the Ash Program Working Group Meeting, Pittsburgh, PA, August 30, 1993.

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