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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT

APRIL-JUNE 1990

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Pittsburgh Energy Technology Center

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This document provides a quarterly status report of the Coal Combustion Science Program that is being conducted at the Combustion Research Facility, Sandia National Laboratories, Livermore, California. The information reported is for the period April-June 1990.

The objective of this activity is to support the Office of Fossil Energy in executing research on coal combustion science. This activity 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 for this activity include:

Task 1: Coal Devolatilization

The objective of this task is to characterize the physical and chemical processes that constitute the early devolatilization phase of coal combustion as a function of coal type, heating rate, particle size and temperature, and gas phase temperature and oxidizer concentration.

The principal investigator on this task is Dr. Thomas H. Fletcher.

Task 2: Coal Char Combustion

The objective of this task is to characterize the physical and chemical processes involved during coal combustion as a function of coal type, particle size and temperature, and gas phase temperature and oxygen concentration.

The principal investigator on this task is Dr. Reginald E. Mitchell.

Task 3: Fate of Mineral Matter During Coal Combustion

The objective of this task is to establish a quantitative understanding of the mechanisms and rates of transformation of mineral matter in coal combustion environments as a function of coal type, particle size and temperature, the initial forms and distribution of mineral species in the unreacted coal, and the local gas temperature and composition. A particular goal is determining the importance of fragmentation in the evolution of the particle size distribution during coal combustion.

The principal investigator on this task is Dr. Larry L. Baxter.

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT APRIL - JUNE 1990

EXECUTIVE SUMMARY

Task 1. Coal Devolatilization

During this quarter, Curie-point desorption in combination with (a) gas chromatography-mass spectrometry (GC-MS) and with (b) direct low-voltage mass spectrometry (LV-MS), was used to investigate the chemical composition and structure of condensed tar vapors produced during rapid devolatilization (heating rate $\sim 10^4$ K/sec) of carefully sized coal particles. Tar samples from the Beulah Zap, New Mexico Blue, Illinois #6, Pittsburgh #8, and Pocahontas #3 seams were collected at different residence times at two gas temperatures (1050 K and 1250 K) using the laminar flow reactor in Sandia's Coal Devolatilization Laboratory (CDL).

GC-MS analyses of the tar samples indicate that the degree of aromaticity increases rapidly as a function of residence time at the 1250 K gas temperature condition. In the 1250 K gas condition, devolatilization is complete within 70 msec, and secondary gas phase reactions of tar vapors (viz. marked increases in PAH content and corresponding decreases in phenolic components) are observed within less than 100 msec. However, at 1050 K the coal devolatilization process appears to be barely complete after 250 msec and little or no evidence of secondary gas phase reactions is found.

Differences in total volatiles yield and particle swelling behavior observed in previous studies in Sandia's Coal Devolatilization Laboratory (CDL) and Char Combustion Laboratory (CCL) may be attributed to one of three independent reactor parameters: (i) gas phase oxygen concentration; (ii) particle heating rate; (iii) and the presence of post-flame combustion gases (H_2O , CO_2 , or radicals such as OH). During this quarter, the effect of gas phase oxygen concentration on particle swelling properties was investigated by adding oxygen to the nitrogen stream in the flow reactor in the CDL. Subsequent pyrolysis studies were performed in the CCL by adjusting the stoichiometry of the post-flame gases to 0% oxygen. The sampling system in the CCL experiments was modified to include a cyclone separation system to prevent tars and soot from recondensing on the char. The sampling locations in each reactor were selected to ensure completion of devolatilization with minimal char oxidation. Future experiments will characterize the effects of heating rate and post-flame combustion products on coal particle swelling during devolatilization.

Results from experiments performed in the CDL at ambient oxygen concentrations from 0 to 10 mole-% oxygen indicate that particle swelling behavior is independent of

the ambient oxygen concentration during coal devolatilization. Pittsburgh #8 coal particles increased in diameter by an average of 50% in the CDL experiments, regardless of gas phase oxygen concentration. Roughly 30-40% of the particles formed transparent, balloon-like cenospheres. Rapid oxidation of these balloon-like cenosphere particles subsequent to coal devolatilization may occur preferentially to oxidation of the thick-walled cenospheres.

The experiments in the CCL show that the absence of oxygen does not affect particle swelling behavior. Balloon-like cenospheres were not observed in the particles collected from the CCL experiments at 0, 6, or 12% oxygen in the post-flame char oxidation region. Total volatiles yields determined from the CDL experiments agree very well with the total volatiles yields from the CCL experiments, except for the low rank coals where some char oxidation may be occurring during the late stages of devolatilization.

Based on the results of the experiments in the CCL and the CDL, it is concluded that gas phase oxygen does not affect particle swelling behavior during coal devolatilization at rapid heating conditions. Reports in the literature of reduced particle swelling during coal devolatilization in oxygen may be attributed to char oxidation subsequent to devolatilization, rather than to chemical changes in softening properties in the early stages of devolatilization. Probable causes for changes in swelling behavior in separate experiments in the CDL and CCL are differences in particle heating rate and /or the presence of post-flame combustion products.

Task 2. The Rates and Mechanisms of Coal Char Combustion

During this quarter, experiments aimed at determining whether the burning rates of coal chars depend upon the conditions under which the chars were formed were continued. Four coals, ranging in volatile matter content from 17% to 62%, are used in the study: Illinois #6 (PSOC-1493D), a hvB-bituminous coal; Blue #1 (PSOC-1445D), a subbituminous coal from New Mexico; Lower Wilcox (PSOC-1443D), a lignite from Texas; and Lower Kittanning (PSOC-1516D), a lv-bituminous coal from Pennsylvania. Three oxygen-level environments were used to produce the chars: an almost oxygen-free environment (50 ppm oxygen), a 6 mole-% oxygen environment, and a 12 mole-% oxygen environment. Gas temperatures during devolatilization were nominally 1700 K.

The apparent densities of the coal chars produced under the different devolatilization conditions were measured. With the higher rank, lower volatile matter-containing coals, the apparent densities of the chars produced in the 50 ppm oxygen environment were greater than those produced in the 6 and 12 mole-% oxygen environments. This may be indicative of early oxidation, some of which could have occurred during the final stages of devolatilization. With the lower rank coals, the apparent densities of the char produced in the different oxygen level environments were essentially the same.

The chars in these experiments will be further characterized to determine their specific surface areas and chemical properties. The chars will then be re-injected into the laminar flow reactor and *in situ* size, temperature, and velocity measurements will be made. The data will be used to determine overall particle burning rates. During this quarter, *in situ* measurements were obtained for the char particles of the Illinois #6 coal that were produced in the three different environments.

Also during this quarter, a model for the apparent density of a coal char particle that accounts for the particle's mineral matter content was derived. The char particle is assumed to consist of two components: a combustible component whose apparent density changes with burnoff and a non-combustible component (the mineral matter) whose apparent density is constant. Such a model is necessary to describe the changes in the apparent densities of particles having high ash contents. Data obtained with Lower Wilcox coal (PSOC-1443D), a high-ash coal, indicate that the char particle apparent density decreases with burnoff during the early to middle stages of burnoff but increases during the late to final stages of burnoff. The apparent density model that is presently used in data analysis (Mitchell, 1987a,b) is not capable of describing this behavior. It is expected that the apparent densities of the chars of all coals increase during the final stages of burnoff when the apparent density of the ash has a pronounced effect on the apparent density of the particle. Thus, such a two-component apparent density model is necessary if the mode of particle burning is to be described accurately during the early to final stages of burning.

Finally during this quarter, analysis of the combustion data obtained with Blue #1 coal (PSOC-1445D) was continued. Blue #1 coal has the lowest ash content (~4% ash on a dry basis) of all the coals studied. Correspondingly, the measured variations in char particle temperatures, a consequence of particle-to-particle variations in ash content, are the narrowest for the Blue #1 coal; the effects of ash on the temperatures the char particles attain during burnoff are minimal. Narrow size and temperature distributions allow effects associated with particle emissivities to be examined. Variations in particle emissivities lead to variations in heat loss rates from particles via radiation, and hence, lead to variations in the apparent chemical reaction rate coefficients determined for particles of the same size and temperature. The *in situ* size and temperature measurements were used to quantify the effects of particle emissivity on the values determined for the kinetic parameters that describe the apparent chemical reaction rate coefficients.

Task 3. The Fate of Mineral Matter

Experiments with a Powder River Basin subbituminous c coal (Smith-Roland; PSOC 1520D) confirm an additional mechanism for mineral matter release that we previously reported. This mechanism was demonstrated using titanium as an example. It was concluded that large portions of atomically dispersed mineral matter is released during coal devolatilization by convective transport of the coal volatiles. During this quarter

similar results were obtained for calcium, magnesium, and sodium. All of these latter elements are strongly implicated in fouling processes of conventional boilers.

Also reported here are the results of experiments aimed at examining the significance of a second mechanism of mineral matter release. Results from tests of a suite of 10 coals in various combustion environments in the Multifuel Combustor (MFC) are summarized. They lend further support to the conclusion that during pulverized coal combustion iron fume is generated from pyritic iron through a process of pyrite decomposition followed by disintegration of the pyrrhotite intermediate. Additional experiments completed this quarter show that this process is sensitive to partial oxidation (ie., room temperature weathering) of the pyrite grains prior to combustion. These results indicate that approximately half of the atomically dispersed mineral matter evolves from coal during coal devolatilization at particle heating rates on the order of 10^5 K/s. Both refractory (Ti, Ca) and volatile (Na, Mg) species show similar trends.

Finally during this quarter, the next set of experiments in the collaborative research effort with Consolidation Coal Company were completed in the MFC. A goal of these experiments is to further develop and validate the Sandia ADLVIC code. ADLVIC allows the prediction of the deposit chemistry in pulverized coal combustors as a function of coal ash properties, operating conditions, and location within the boiler or combustion residence time

Future Work

During the next quarter, NMR analyses of char particles and condensed tar samples from the CDL for additional coals will be completed. Preliminary tests will be conducted to determine the feasibility of performing gas species analyses in the CDL with minor modifications. These tests include the use of Fourier Transform Infrared Spectroscopy (FTIR) with a 20 m path length cell. The results of the MS and NMR analyses indicate the need for sampling of tars and chars at a new gas condition (1150 K) and at longer residence times in the 1050 K gas condition. An 1150 K gas condition will be characterized during the next quarter, and samples will be obtained for one coal at this condition and at longer residence times in the 1050 K gas condition. In addition, the development of the chemical percolation devolatilization (CPD) model will continue.

Also, during the next quarter analysis will continue of the combustion data from the CCL to determine kinetic parameters for the chars of the various coals tested. As suggested by the analysis described in this report, average values of char particle emissivities, determined at various extents of burnoff, will be employed. To assure that this approach yields an activation energy for the char oxidation reaction that is representative of all particles, separate emissivity ranges will be analyzed as well. In addition, *in situ* size, temperature, and velocity measurements using the chars that were produced under different devolatilization conditions will continue in the CCL. These data will be used to determine to what extent the apparent burning rates of coal

chars depend upon the devolatilization conditions. Also, the chemical analyses of the chars collected at various extents of burnoff will commence during the next quarter. Data analysis will yield the release rates of sulfur and nitrogen from the char during burnoff for the various coals examined.

Data packages containing all the data obtained in the various combustion tests for each of the coals examined are being compiled. To date the packages contain the *in situ* size, temperature, and velocity measurements and the m/m_0 and apparent density measurements at each sampling height in each of the gaseous environments employed. During the next quarter, the chemical analyses of the chars collected will be included. The completed packages will contain the results of data analyses as well.

Finally, during the next quarter experiments will be completed to determine mineral matter evolution from the matrix of test coals in the Multifuel Combustor. Experiments in the MFC will also be extended to examine the effect of weathering of the raw coal on the release of iron fume during combustion, and to provide additional data for and validation of the Sandia ADLVIC model.

PROJECT TITLE: COAL COMBUSTION SCIENCE
TASK 1: COAL DEVOLATILIZATION
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CONTRACT: FWP 0709
REPORTING PERIOD: April 1 - June 30, 1990
REPORTED BY: T. H. Fletcher and D. R. Hardesty
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OBJECTIVE FOR TASK 1

The objective for Task 1 is to characterize the physical and chemical processes that constitute the early devolatilization phase of coal combustion as a function of coal type, heating rate, particle size and temperature, and gas-phase temperature and oxygen concentrations.

These objectives are met by conducting basic research in three Subtask areas as follows:

Subtask 1.1 Pyrolysis Product Compositions and Heating Values

The goal of this subtask is to consider and implement schemes that will permit measurement of tar yields and gas compositions in the existing apparatus. Plans include analysis for major species such as CH₄, CO, CO₂, C₂H₆, C₂H₄, and H₂O using standard gas chromatographic and/or Fourier transform infrared (FTIR) spectroscopic techniques. In addition, it may be possible to use an on-line mass spectrometer for tar analysis and for identification of species containing nitrogen. The heating values of a few of the chars from devolatilization experiments will be measured and compared with published correlations that are principally based on raw coals. Optical experiments will also be performed using the pyrometry system in an attempt to lower the temperature detection threshold below the current 850 K for a 100 μm particle.

Subtask 1.2 Chemical Structure of Coal During Devolatilization

In a collaboration with the Nuclear Magnetic Resonance (NMR) Laboratory at the University of Utah through the Advanced Combustion Engineering Research Center (ACERC), research includes investigation of the chemical structure of the parent coals as well as the chemical structure of the tar vapors and char particles produced in rapid heating devolatilization experiments. Initial data collected in FY89 for two coals (PSOC-1493D and 1508D) will be analyzed and supplemented with NMR

measurements for additional samples derived from these two coals. Investigations of chemical structure will continue in FY90 on other coals, including low rank coals (e.g., PSOC-1507D North Dakota Zap lignite and PSOC-1445D New Mexico Blue subbituminous coal) and bituminous coal (e.g., PSOC-1451D HVA bituminous coal). The focus of the NMR analyses will be the quantitative identification of functional groups in a manner that permits comparison with current devolatilization models, such as the chemical percolation devolatilization (CPD) model. The goal is to provide a devolatilization model simple enough to use in large coal combustor simulations, while describing the devolatilization process and product distribution in some detail. Development of the CPD model will continue as more data are generated, including meaningful ways to model molecular weight distribution and transport effects.

Subtask 1.3 Transition from Coal Devolatilization to Char Combustion

The transition from pulverized coal devolatilization to char combustion will be studied by (a) operating the Coal Devolatilization Laboratory with 0-10% oxygen, and (b) operating the Coal Combustion Laboratory (CCL) with 0% post-flame oxygen. The solids sampling system in the CCL will be modified to separate char particles from tars and aerosols. Particles will be examined for elemental composition (C, H, N, O, and S), physical structure (using optical and electron microscopy), apparent density, diameter, and internal surface area. The extent of mass release will be determined from tracer elements in the ash (Si, Al, and Ti) in a manner similar to previous studies. In addition, the chars collected from the different gas environments will be reinjected into the CCL, and apparent burning rates will be determined. The results of the experiments studying the transition from coal devolatilization to char oxidation will be combined with theoretical studies involving existing devolatilization and char combustion models.

SUMMARY OF TECHNICAL PROGRESS DURING THIS QUARTER

Research this quarter focused on analyzing the mass spectrometry data for tars from the Coal Devolatilization Laboratory (CDL). The mass spectrometry analyses were performed at the University of Utah in conjunction with Professor Henk Meuzelaar. These results will appear in the preprints to the National Meeting of the American Chemical Society, Division of Fuel Chemistry, to be held in Washington, D. C., August 26-31, 1990.

Also included in this quarterly report are the results of experiments performed in the CDL and in the Char Combustion Laboratory (CCL) to determine the effects of gas phase oxygen concentration on particle swelling and yields during devolatilization. A small literature review of previous research is presented along with these results.

Subtask 1.1 Pyrolysis Product Compositions and Heating Values

Tar samples collected for five coals (PSOC-1445D, 1451D, 1493D, 1507D, and 1508D) at different residence times in the CDL were analyzed by mass spectrometry in collaboration with Professor Henk Meuzelaar at the University of Utah. This section describes the results of the mass spectrometry (MS) analyses.

Introduction

Recent devolatilization studies (Fletcher, 1989; Solomon, et al., 1986; Freihaut and Proscia, 1989; Gibbins-Matham and Kandiyoti, 1988; Serio, et al., 1987) have identified the rates and the temperature regimes of pulverized coal devolatilization as a function of heating rate, final temperature, and coal type. Careful particle temperature measurements during devolatilization at rapid heating conditions (Fletcher, 1989; Solomon, et al., 1986) have eliminated many uncertainties caused by estimations of particle temperatures in early studies.

Current devolatilization models have advanced beyond one-step Arrhenius kinetics to descriptions of the bonding structure in the coal, metaplast, and tar (Niksa and Kerstein, 1986; Solomon, et al., 1988; Grant, et al., 1989; Fletcher, et al., 1990a). Other models include detailed empirical correlations to estimate yields of tar products from elemental compositions of the parent coal (Ko, et al., 1988), as well as a mechanism to describe the evolution of the physical structure of char particles (Oh, et al., 1989). Most of these models presume a mechanism for generation of metaplast during pyrolysis, followed by release of lighter fractions of the metaplast as tar vapor, where tar is commonly defined as pyrolysis products that condense at room temperature and pressure. It is clear that quantitative experimental investigations of the evolution of the chemical structure of solid and condensible pyrolysis products (char and tar) are critical to the understanding of coal devolatilization mechanisms.

The present study addresses the characterization of condensible tar vapors, produced by rapid ($\sim 10^4$ K/sec) heating of pulverized coals in a laminar flow reactor. Curie-point desorption GC/MS and direct low-voltage MS methods were used to characterize tar samples at the molecular level and to elucidate some of the underlying reaction mechanisms. Results are compared qualitatively with analyses of the same tars by ^1H and ^{13}C NMR spectroscopy (Fletcher, et al., 1990b).

Experimental Approach

a. Reactor and Sample Collection System

Condensed tar vapors from rapid devolatilization (heating rate $\sim 10^4$ K/sec) of carefully sized coal particles were collected on polycarbonate filters in Sandia's Coal Devolatilization Laboratory. Tars from the following coals were examined: Beulah Zap lignite (PSOC-1507D), New Mexico Blue subbituminous (1445D), Illinois #6 hvb bituminous (1493D), Pittsburgh #8 hva bituminous (1451D), and Pocahontas #3 lv

bituminous (1508D). Tar samples were obtained as a function of residence time at the 1050 K and 1250 K gas conditions using techniques described by Fletcher (1989). The sampling system included a water-cooled, helium-quench probe to collect solid samples isokinetically, and a virtual impactor and three-stage Andersen cyclone system to aerodynamically separate char particles from condensed tar vapors and aerosols. Tar samples were stored at temperatures below 273 K until analysis (including the time of transport to the University of Utah).

b. Curie-Point GC/MS and Low-Voltage MS Analyses

Analyses of the tar samples by GC/MS were performed at the University of Utah's Center for Micro Analysis and Reaction Chemistry under the direction of Professor Henk Meuzelaar. The analyses were performed using a Hewlett Packard 5890 chromatograph with a 15 m x 0.25 mm i.d. x 0.25 μ m film thickness DB-5 column (J&W Scientific). A schematic of the Curie point GC/MS system is provided in Fig. 1.1a. The conditions used in GC/MS were as follows: electron energy 70 eV, ion trap detector (ITD, Finnigan MAT) scanned from m/z 40-450 at 1 scan/sec, pyrolysis time 2 sec, 883K Curie-point wires in an inlet set at 523 K. The column was temperature programmed from 313-573K at 15 K/min.

Low-voltage MS experiments were carried out using an extranuclear Model 5000-1 Curie-point pyrolysis MS system (see Fig. 1.1b). Twenty-five microgram quantities of tar were coated on ferromagnetic wires from methanol suspensions. The wires were inserted into borosilicate glass reaction tubes and introduced into the vacuum system of the mass spectrometer. The ferromagnetic wires were inductively heated at approximately 100 K/s to an equilibrium temperature of 883 K. Total heating time was 10 sec. Low-voltage MS conditions were as follows: electron ionization at 12 eV (set value), scanning rate 1000 amu/s, total scanning time 20 s, mass range scanned m/z 40-260.

Results and Discussion

a. Curie-Point Desorption Low-Voltage Mass Spectrometry Analyses

Low-voltage mass spectra of tars obtained by Curie-point desorption directly in front of the ion source are shown in Fig. 1.2a-e for two different coals. Beulah Zap tar samples obtained in the 1250 K gas condition at 70 ms and 250 ms are compared in Figs. 1.2a and 1.2b. Comparison of these two samples shows (1) a marked decrease in hydroxyaromatic signals (e.g., alkylsubstituted phenols, dihydroxybenzenes, and naphthalenes) accompanied by (2) a strong increase in polycondensed aromatic hydrocarbons (e.g., phenanthrenes and pyrenes) in the 250 ms sample (organic structures are illustrated in Fig. 1.3). The marked change in the nature of the tars collected at 70 and 250 ms is attributed to secondary reactions of tar in the gas phase, subsequent to release from the coal particle. Especially significant is the dominance of unsubstituted pyrene among the various alkylsubstituted homologs. This is a telltale

Figure 1.1a Schematic of the Curie-point desorption GC/MS system

Figure 1.1b Schematic of the Curie-point desorption LV/MS system.

Figure 1.2 Curie-point desorption mass spectra of Beulah Zap and Pittsburgh #8 tars showing the effects of coal rank (a and b vs c, d, and e), residence time (a and c vs. b, d, and e) and gas temperature (e vs. a, b, c, and d).

Figure 1.2e Curie-point desorption mass spectra of Pittsburgh #8 tar from the 1050 K gas condition. Compare with Figures 1.2a, b, c, and d.

alkyl phenol

dihydroxybenzene

naphthalenes

anthracene

phenanthrene

pyrene

perylene

picene

terpene

Figure 1.3 Structures of organic compounds referred to in Task 1.

sign of high temperature gas phase reactions and may perhaps be seen as a first step in the direction of soot formation.

The Beulah Zap tar pattern at 70 ms, on the other hand, compares well with direct Curie-point pyrolysis mass spectra of North Dakota coal (Metcalf, et al., 1987). This indicates that at 70 ms, primary pyrolysis products (e.g., dihydroxybenzenes) still dominate, although the yield of polycondensed aromatic hydrocarbons (e.g., alkyl phenanthrenes) is already higher than would be observed under vacuum micropyrolysis conditions.

The tar patterns of Pittsburgh #8 coal at 1250 K (Figs. 1.2c and d) are in excellent agreement with the observations from tars from the Beulah Zap lignite. The short residence time pattern (80 ms) corresponds quite well with the Curie-point pyrolysis mass spectrum (as reported by Chakravarty et al., 1988), whereas the long residence time (250 ms) tar shows a pronounced shift towards polycondensed aromatic hydrocarbon. Due to the higher rank (high bituminous) of the Pittsburgh #8 coal, however, the short residence time spectrum (Fig. 1.2c) is clearly different from that of the Beulah Zap lignite. For example, the tar from the Pittsburgh #8 coal exhibits lower (alkyl) dihydroxybenzene intensities and increased (alkyl) naphthalene series than tar from the Beulah Zap lignite. This is in agreement with trends observed in earlier LV-MS studies of coals of different rank (Meuzelaar, et al., 1984).

Finally, the effect of temperature is briefly illustrated by comparison of Figs. 1.2c and 1.2e (Pittsburgh #8, 70 ms at 1250 K vs. 250 ms at 1050 K). In spite of the long residence time (250 ms), the MS pattern in Fig. 1.2e is highly similar to that in Fig. 1.2c, indicating the absence of marked secondary reactions at this lower temperature.

b. Curie-Point Desorption Gas Chromatography/Mass Spectrometry Analyses

The Curie-point desorption GC/MS technique confirms and further elucidates the trends observed in the LV/MS analyses, as illustrated in Figs. 1.4 and 1.5. Illinois #6 tar sampled at 250 ms (Fig. 1.5) in the 1250 K gas condition shows an approximate 100-fold reduction in the relative abundance of (alkyl) phenols (intensities in left-hand panels of Fig. 1.5 are multiplied by 100) relative to the tar sampled at 70 ms. A corresponding ten-fold increase in selected polycondensed (4-6 ring) aromatic hydrocarbons is observed in the 250 ms sample (compare scaling factors of right-hand panels of Figs. 1.4 and 1.5).

Changes in relative composition as a function of residence time are illustrated for New Mexico Blue tars at 1050 K in Fig. 1.6 and for Beulah Zap, Illinois #6, and Pittsburgh #8 tars in Figs. 1.7a, b, and c, respectively. At 1050 K, fragment ions of aliphatic hydrocarbons (e.g., at m/z 85, 57, 43, in Fig. 1.6c) dominate the short residence time (120 ms) tar. Based on previous, time-resolved pyrolysis field ionization MS studies (Yun, et al., 1990), early evolution of aliphatic hydrocarbon moieties during devolatilization of low-rank coals is likely to represent the desorption

of low MW biomarker-type compounds (e.g., branched and/or alicyclic terpenoids). At 150 ms the relative intensities of the aliphatic hydrocarbon moieties start to decrease due to the strong increase in hydroxyaromatics (e.g., dihydroxybenzenes at m/z 110 and 124, Fig. 1.6b). At 250 ms, the relative abundance of compounds such as naphthols are still increasing, suggesting that the devolatilization process may not yet be fully completed. However, suspected secondary reaction products such as pyrenes and perylenes are starting to increase slightly. Nevertheless, the relative abundance of the highly reactive dihydroxybenzenes appears to be more or less stable. Altogether, the conclusion is that at 1050 K the devolatilization process of New Mexico Blue coal is close to being complete after 250 ms.

A much different picture is obtained at 1250 K, as illustrated for the three coals in Fig. 1.7. Concentrations of compounds such as pyrenes, perylenes, and even picenes appear to increase continuously after the first sampling position, whereas the relative abundances of naphthols and even phenanthrenes decrease after approximately 100-150 ms. This is further evidence of marked secondary gas-phase reactions. The above observations at 1050 and 1250 K suggest that devolatilization at 1150 K should be completed within 100-200 ms, and that the onset of secondary gas-phase reactions should become clearly visible at longer residence times. A set of experiments will be performed during the next quarter to collect and analyze tar and char samples at (a) an 1150 K gas condition, and (b) longer residence times in the 1050 K gas condition.

c. Comparison with ^1H and ^{13}C NMR Analyses

The same tars examined in this study were analyzed previously by ^1H and ^{13}C NMR spectroscopy (Fletcher, et al., 1990b). The NMR data indicate that tars evolved from the Illinois #6 coal are similar in chemical structure to the parent coal. In the 1250 K gas condition, the NMR data indicate that tar reacts in the gas phase, while little or no evidence of gas phase reaction of tars is indicated in the 1050 K gas condition. The tar samples collected at long residence times (250 ms) in the 1050 K gas condition were similar in chemical structure to the initial tar evolved in the 1250 K gas condition (70 ms). The tar samples collected at long residence times (250 ms) in the 1250 K gas condition exhibited: (1) a decrease in 1-ring aromatic compounds; (2) an increase in aromatic ring compounds with 3 or more rings; (3) an increase in the carbon and proton aromaticity (at the expense of aliphatic material); and (4) a decrease in the aliphatic carbons in the β and γ positions relative to the aromatic rings.

The LV/MS and GC/MS data presented here are consistent with the NMR data, and show further detail regarding gas phase reaction of specific organic compounds in the tar. For example, one ring compounds indicated in the MS analyses of the tars are alkyl phenols and dihydroxybenzenes; these compounds were shown to decrease in abundance in the long residence times in the 1250 K gas condition. Similarly, the MS data for tar samples collected at long residence times in the 1250 K gas condition indicate an increase in polycondensed aromatic compounds with 3 or more aromatic rings, such as phenanthrenes and pyrenes. The detail provided by the MS analyses

(a) NEW MEXICO BLUE (1050 K)

(b) NEW MEXICO BLUE (1050 K)

(c) NEW MEXICO BLUE (1050 K)

Figure 1.6 Relative abundance of selected ion profiles in Curie-point desorption GC/MS data on New Mexico Blue tar samples obtained in the 1050 K gas condition at different residence times.

Figure 1.7 Same as Fig. 1.6 but representing tars from three different coals obtained in the 1250 K gas condition.

helps to interpret the coarse but quantitative chemical groups identified in the NMR analyses.

Conclusions

Based on the Curie-point GC/MS and low-voltage MS analyses of the tar formed during devolatilization of Beulah Zap, New Mexico Blue, Illinois #6, Pittsburgh #8, and Pocahontas #3 coals, the following conclusions are reached:

1. The degree of aromaticity increases rapidly in tars from all five coals as a function of residence time at the 1250 K gas temperature. However, little increase in aromaticity in the tars is detected at the 1050 K gas temperature.
2. At a gas temperature of 1250 K, devolatilization is complete within 70 msec and secondary gas-phase reactions of tar vapors can be observed within 100 msec. At 1050 K, the devolatilization process appears to be more or less complete after 250 msec.
3. In order to study the complete devolatilization process and the possible onset of secondary reactions, further experiments should be conducted at an intermediate temperature, e.g., 1150 K.

These conclusions are consistent with the ^1H and ^{13}C NMR analyses performed previously on these same tars (Fletcher, et al., 1990b).

Subtask 1.2 Chemical Structure of Coal During Devolatilization

Considerable progress has been made in analyzing the chemical structure of coal chars during devolatilization. ^{13}C NMR experiments for two additional coals have been performed, and the data is currently being analyzed. These NMR data will appear in the next quarterly report, and will also appear in a paper entitled: "Structural Evolution of Matched Tar/Char Pairs in Rapid Pyrolysis Experiments," by R. J. Pugmire, M. S. Solum, D. M. Grant, S. Critchfield, and T. H. Fletcher. This paper will be presented by Dr. Pugmire at the International Conference on Coal Structure and Reactivity, Queens College, Cambridge, UK (September 5-7, 1990); all papers from this conference will be submitted jointly for publication to *Fuel*.

Significant improvements have recently been made in the chemical percolation devolatilization (CPD) model. New developments include a plug flow formulation for the vapor-liquid equilibrium scheme, incorporation of a crosslinking mechanism, selection of additional model input parameters from NMR data, and independent comparison of model predictions with chemical structure data (from the NMR analyses of char samples) as a function of residence time. These refinements to the model are currently in progress, and results will appear in the next quarterly report.

Subtask 1.3 Transition from Coal Devolatilization to Char Combustion

Introduction

Coal devolatilization affects the combustion performance of pulverized fuel boilers in many different ways. The primary influences of coal devolatilization on combustion performance are the amount of mass released as volatile matter and the heating value of the pyrolysis products. The volatile matter is released quickly compared to the subsequent heterogeneous char oxidation, and significantly influences near-burner gas temperatures and stoichiometry. Equally important is the amount of mass remaining in the char, since this is the mass that must be oxidized in the available residence time in the furnace. The physical structure of the char subsequent to devolatilization (i.e., internal surface area, pore size, and porosity) determines the rate of char oxidation. Many devolatilization experiments have been conducted at moderate temperatures (800 to 1300 K) and moderate heating rates (10^3 to 10^4 K/s), since this regime allows definition of primary devolatilization products and rates of evolution. At higher temperatures and heating rates, the primary devolatilization products decompose in the gas phase. Secondary devolatilization products formed from gas phase decomposition of primary volatiles include additional light gases as well as soot. In order to understand the transition from coal devolatilization to char oxidation, the effect of high temperatures (1300 to 2000 K) and rapid heating rates ($> 10^5$ K/s) on devolatilization must be characterized.

Coal particle swelling must be understood as a function of heating rate and temperature before a description of the transition from coal devolatilization to char oxidation can be completed. As high volatile bituminous coals are heated, the aliphatic bonds between the aromatic clusters are broken, and fragments are formed with small enough molecular weight to become liquid. The liquid in the coal is termed metaplast. Further increases in temperature raise the vapor pressures of the lower molecular weight species in the metaplast, and tar vapor is released from the particle. Light gases are formed from the aliphatic bridge material. High volatile bituminous coals contain enough metaplast for the particle to exhibit liquid properties in certain temperature regimes. As internal gases (light gases and tar vapors) are generated, bubbles are formed. With sufficient bubble formation, the internal pressure becomes larger than the surface tension of the particle, and the particle diameter increases. In low rank coals, crosslinking reactions scavenge much of the metaplast before it can be released as tar, and no particle swelling is observed.

The degree of particle swelling during devolatilization may affect the particle temperature in a practical coal combustion system; thermal radiation to the particles is significant in large combustors. Heat transfer to and from particles is a function of the particle surface area, which is proportional to the square of the particle diameter. Particle size, density, and internal surface area also significantly affect the rate of char oxidation. Small particles may burn in a regime where oxygen penetrates the pores of the particles (Zone I), and hence the reaction rate is controlled by the intrinsic

chemical reactivity of the char.. Intermediate size particles may burn in a regime where time scales of internal diffusion of oxygen through the pores and the intrinsic chemical reactivity are of the same order (Zone II). Large particles may burn in a regime where the rate is controlled by the diffusion of oxygen to the particle surface from the ambient gas stream (Regime III).

The physical properties of a coal char are rank dependent. Chars from low rank coals do not swell, and exhibit high internal surface areas. Chars from bituminous coals may soften, resulting in large internal voids caused by bubbles in the particle during pyrolysis. The large internal voids generated in softening coals reduce the diffusion resistance in the particle in Zone II combustion conditions, although for simplicity most char combustion studies assume a continuous pore structure throughout the particle.

In an oxidizing atmosphere, devolatilized gases and tar vapors combust with the oxygen. At rapid heating conditions typical of pulverized fuel furnaces, the mass release from the particle is high enough to reduce the amount of heat transfer to the particle (particle blowing). The oxygen is partially consumed by combustion with the volatiles, and the mass flux of volatiles is large enough to prevent diffusion of oxygen to the surface. However, during the late stages of devolatilization, the mass flux is not as high, and it is therefore possible that oxygen may react heterogeneously with the char before complete devolatilization.

The purpose of this study is to investigate the transition from coal devolatilization to char oxidation, including the differences in the physical and chemical char structures formed during devolatilization and combustion experiments. This study also includes investigation of the total mass release attributable to devolatilization as a function of temperature, and possible regimes where devolatilization and char oxidation at rapid heating conditions may occur simultaneously.

In the following section, a literature review of previous research on high temperature devolatilization yields and particle swelling behavior is presented, followed by a summary of previous work at Sandia in the CDL and CCL. Finally, results of new experiments completed during this quarter in the CDL and CCL in different gas phase oxygen environments are presented.

Background

a. High Temperature Coal Devolatilization ($T_p > 1300$ K)

Many coal devolatilization experiments have been conducted at temperatures less than 1300 K. However, relatively few detailed studies of devolatilization have been performed at temperatures higher than 1300 K. The results of experiments performed without an aerodynamic separation of tars and soot from char particles (e.g., Kobayashi, et al., 1976; Ubhayakar, et al., 1976) are questionable, since the redeposition of pyrolysis products onto the char makes interpretation difficult.

Wornat, et al. (1987) studied the soot/tar ratio from a bituminous coal at temperatures ranging from 1100 to 1500 K; total mass release was not reported as a function of temperature. Serio, et al. (1987) reported volatiles yield for a lignite at 1073 K (V=55% daf) and 1873 K (V=68% daf), although the lignite was not held at 1073 K long enough to achieve complete devolatilization. The most notable high temperature products from the 1873 K experiment were CO and H₂. Kimber and Gray (1967) used a plasma torch for a heat source in a drop tube furnace with graphite resistance heaters for walls. Samples were collected in a water cooled probe equipped with a cyclone separator. The total volatiles yields (% daf) reported for a low rank coal were 48% at 1370 K, 60% at 1720 K, and 72% at 2170 K.

Tamhankar, et al. (1984) used a modified thermogravimetric analyzer (TGA) to study the pyrolysis behavior of lignite at heating rates ranging from 100 to 1000 K/s and temperatures between 973 and 1873 K for a lignite in N₂, CO₂, and H₂O. A plateau in the volatiles yield was observed at 1473 K, followed by additional rapid rise at 1473 K. Morgan and Dekker (1987) used a drop tube to measure volatiles yields for three coals (hvb, mvb, lvb) at 1473, 1673, and 1773 K. A gas quench probe and a cyclone separator were used in these experiments. Residence times were estimated at 80 ms maximum. All three coals showed increase in yield at each increase in temperature. Blair, et al. (1976) studied nitrogen evolution from coal using a graphite ribbon. The experiments were conducted at high heating rates, with temperatures ranging to 1400 K. The data show increases in yield with increasing temperature for Illinois #6, Wyodak and one other coal. Pohl and Sarofim (1976) used an entrained flow reactor and a crucible heater to examine nitrogen evolution during pyrolysis. Temperatures as high as 2300 K were achieved in their experiments. Continual increases in yield with temperature were observed for a bituminous coal and a lignite.

b. Particle Swelling Behavior

Lightman and Street (1968; Street, et al., 1969) examined the characteristics of chars from pyrolysis of high volatile bituminous coals in a drop tube furnace with air or nitrogen as the carrier gas. Their findings indicated a sequence of swelling that included: (i) fissures in the particles (~573 K); (ii) larger fissures, with internal gas bubbles evident (~723 K); (iii) large interconnected internal voids, with surface bubbles apparent (~773 K); (iv) ignition (~913 K). They classified the particles into four categories: (a) relatively solid particles with fissures and ash sandwiches; (b) lacy cenospheres with many internal partitions; (c) thin-walled balloons; and (d) thick walled cenospheres. Particles treated in nitrogen possessed a more open structure and were more swollen than those treated in air. Swelling was shown to be influenced by the duration and temperature of treatment. Swelling ratios were obtained for four different coals, with furnace temperatures of 1073 K, as summarized in Table 1.1.

The data for the bituminous coal (Ackton Hall) indicate 57% diameter change when particles were heated in nitrogen, but only 10% diameter change when heated (and combusted) in air. The lower rank coal (Rawdon) exhibits less diameter change due

Table 1.1
Summary of Swelling Data from Lightman and Street (1968)

Coal	Size (μm)	B.S. Swelling Number	Swelling Ratio	
			Air	Nitrogen
Rawdon	63-75	1/2	1.04	1.16
	53-63			
Ackton Hall	24-30	5	1.09	1.57
	53-63		1.10	
	90-105		1.09	
Grange Ash	53-63	8	1.16	
Yniscedwyn	63-63	0	1.00	

to heating in the nitrogen environment. These data suggest that the devolatilization of coal in oxidizing atmospheres may inhibit particle swelling for bituminous coals.

Tsai and Scaroni (1987) studied the structural changes in bituminous coal particles heated in a drop tube furnace to 1200 K (estimated heating rate of 10^4 K/s). Data were presented for 112 μm diameter particles heated in nitrogen and in air. Diameter increases were determined by combining measurements of apparent density (tap density technique) with measurements of mass release (ash tracer technique). Pyrolysis in nitrogen showed a swelling region with particle diameter increases of up to 20%, followed by shrinkage region with subsequent decreases in diameter of approximately 10%. In the combustion tests with the same coals, the swelling was more pronounced (up to 30% swelling), with subsequent large extents of shrinkage (partially due to combustion). The internal particle surface area was characterized by CO_2 adsorption. Particles heated in air and in N_2 exhibited identical changes in internal surface area as a function of mass release, until the onset of char oxidation in the combustion experiment.

Melia and Bowman (1983) suggested a three zone model for particle swelling during devolatilization: (1) a rigid coal matrix; followed by (2) a low viscosity plastic state; followed by (3) a rigid char matrix. Their model suggests that the extent of swelling is dependent on particle heating rate. At low heating rates (~ 1 K/s), little swelling occurs, while maximum swelling occurs at heating rates of 10^4 to 10^5 K/s. At even higher heating rates, little swelling occurs. This model relies heavily on data obtained by Pohl, et al. (1978), where particle diameter increases of 1000% were reported. Diameter increases reported in the literature are generally less than 100%; larger diameter increases may have been caused by particle agglomeration.

c. Previous Research at Sandia

Recent coal combustion research at Sandia includes both devolatilization experiments and char oxidation experiments. The goal of this research effort is to describe the reaction behavior of coal particles throughout their lifetime in a typical pulverized coal-fired boiler. The devolatilization experiments have been conducted in 100% nitrogen to isolate the pyrolysis reactions, with typical particle heating rates of 10^4 K/s and particle temperatures as high as 1200 K. The char combustion experiments have been conducted in oxidizing environments (6-12 mole-% oxygen) after the pyrolysis process is complete, with minimum particle heating rates of approximately 10^5 K/s and particle temperatures of approximately 1500 K. In order to adequately describe combustion behavior in a large scale system, it is important to bridge the gap between the devolatilization experiments and the char oxidation experiments.

Common coal samples were used in the coal devolatilization and char oxidation experiments. The coals were sieved in a nitrogen environment and then aerodynamically classified using a Vortec cyclone system. Particles were fed to the respective reactors at approximately 10 mg/min in order to ensure single particle behavior. Partially pyrolyzed chars were obtained in the pyrolysis reactor in the Coal Devolatilization Laboratory (CDL) as a function of residence time using a helium quench probe. Helium transpires through a porous inner liner in this probe to minimize tar deposition. The sampling system in the CDL includes an aerodynamic virtual impactor and cyclone system to separate tar aerosols from char particles. The chars were collected in the laminar flow reactor in the Coal Combustion Laboratory (CCL) using a helium quench probe and a filter to collect char particles. Previous to the current experiments, the collection system in the CCL, however, did not include the porous probe liner, the virtual impactor, or the cyclone system; tars and soot completely burn before the first sampling position in normal char oxidation experiments.

Char samples collected in the two laboratories were analyzed for organic and inorganic elemental composition. The ratio of the apparent density of the char sample to that of the parent coal was measured using a tap density technique (described in earlier quarterly reports). The mass mean diameter of the char sample was determined from the combination of the extent of mass release and the apparent density, using the following relationship:

$$\left(\frac{\rho}{\rho_o}\right) \left(\frac{d}{d_o}\right)^3 = \left(\frac{m}{m_o}\right), \quad (1.1)$$

where d is the particle diameter, m is the mass of the particle, ρ is the apparent density of the particle, and the subscript o refers to the parent coal sample.

The results of previous experiments in the CDL and the CCL are summarized in Table 1.2, where V represents the percentage of mass release from the particle (volatile yield) expressed on a dry, ash-free (daf) basis. The numbers presented in

Table 1.2
Comparison of Mass Release and Particle Swelling in the CCL and CDL
Experiments at Sandia

a. PSOC-1451D, 106-125 μm (Pittsburgh hva bituminous)

Reactor	Condition	m/m_0 (dry)	ρ/ρ_0	d/d_0	V (% daf)
CDL	1250 K	0.59	0.20	1.44	45
CCL	6% O ₂	0.50	0.38	1.10	55
	12% O ₂	0.50	0.39	1.08	55

b. PSOC-1493D, 106-125 μm (Illinois #6 hvb bituminous)

Reactor	Condition	m/m_0 (dry)	ρ/ρ_0	d/d_0	V (% daf)
CDL	1250 K	0.54	0.36	1.14	52
CCL	6% O ₂	0.48	0.52	0.97	59
	12% O ₂	0.49	0.47	1.01	59

c. PSOC-1445D, 106-125 μm (New Mexico Blue subbituminous)

Reactor	Condition	m/m_0 (dry)	ρ/ρ_0	d/d_0	V (% daf)
CDL	1250 K	0.48	0.32	1.14	54
CCL	6% O ₂	0.49	0.46	1.02	56
	12% O ₂	0.49	0.39	1.08	56

this table differ slightly from those presented in the January-March 1989 Quarterly Report (Fletcher and Hardesty, 1989); the m/m_0 determination previously reported was taken solely from mass balance measurements rather than from tracer analysis. The data indicate that the apparent densities of the coal particles from the CDL experiments are lower than in the corresponding CCL experiments, particularly for the Pittsburgh #8 coal.

The average diameter change calculated from the apparent density measurements and the mass release determinations shows 44% swelling for the Pittsburgh #8 coal in the CDL, compared to only 10% swelling in the CCL. The swelling indicated by the other two coals is also greater in the CDL than in the CCL. The Pittsburgh #8 coal is a softening coal, and is expected to exhibit the most dramatic swelling behavior,

whereas the subbituminous coal should exhibit the least amount of swelling for the three coals tested.

The mass release V was 4-20% higher in the CCL than in the CDL. The 45% yield shown in this table for the Pittsburgh #8 coal was from some early experiments in the CDL. In subsequent experiments in the CDL using a smaller size fraction of the same coal (PSOC-1451D, 63-75 μm), performed after improvements in the sampling and analysis techniques, the measured extent of mass release was 53% (daf). This yield compares favorably with the 55% mass release measured in the CCL experiments for the 106-125 μm diameter particles, and may indicate that there is not a substantial difference in mass release between the experiments conducted in the CDL and in the CCL.

Approach to the Present Experiments

The differences in swelling behavior between experiments conducted in the CDL and the CCL are attributed to three independent reactor parameters: (a) gas phase oxygen concentration; (b) particle heating rate; and (c) the presence of post-flame combustion products (i.e., H_2O , CO_2 , and radicals such as OH). The experiments described here were performed to investigate the effects of gas phase oxygen concentration on coal particle swelling behavior during devolatilization. In particular, the effect of oxygen was studied by performing experiments in the CDL with controlled amounts of oxygen added to the nitrogen environment, and by performing experiments in the CCL with little or no oxygen present in the post-flame environment. The particle temperature histories in the two flow reactors were not changed significantly by adding or subtracting oxygen. Future experiments will characterize the effects of heating rate and post-flame combustion products on coal particle swelling during devolatilization.

The experiments in the CCL with no post-flame oxygen required modifications to the sampling system to aerodynamically separate tars, soot and aerosols from char particles. The cyclone from the CDL was therefore used in these experiments to prevent the tar and soot from recondensing on the char particles. The extent of mass release from the char particles was determined from the trace mineral species (Si, Al, Ti, and total ash), and the apparent density was determined as described above. Samples were obtained in the CDL at two different residence times in the 1250 K gas condition: 130 ms (subsequent to tar release) and 250 ms (reactor exit). Samples were taken just subsequent to the pyrolysis zone (47 ms, 6.4 cm above the burner) in the CCL. Maximum gas temperatures in the CCL experiments were approximately 1600 K, corresponding to the temperatures used in previous char combustion experiments.

Results

a. Total Volatiles Yield

The total volatiles yield data from the experiments performed in the CDL and in the CCL are shown in Table 1.3 for five different coals. The percentage of oxygen in the parent coal is used as an indicator of rank. The terms CCL-0, CCL-6 and CCL-12 denote experiments in the CCL with 0, 6, or 12% oxygen in the post flame gas. All of the data shown for CCL-6 and CCL-12 were obtained for the size fraction 106-125 μm . The 106-125 μm size fraction was also used for the CDL-0 and CCL-0 experiments on PSOC-1445D, 1493D, and 1508D. In the CDL-0 and CCL-0 experiments, however, due to insufficient quantities of the 106-125 μm size fraction, the 75-106 μm size fraction of PSOC 1507D and the 63-75 μm size fraction of PSOC-1451D were used.

Table 1.3
Comparison of Total Volatiles Yields in the CDL and CCL Experiments

Coal Type (PSOC-)	Oxygen (% daf)	ASTM V (% daf)	CDL-0 V (% daf)	CCL-0 V (% daf)	CCL-6 V (% daf)	CCL-12 V (% daf)
1507D	25.2	49.6	53.7	58.6	61.7	61.7
1445D	16.3	46.8	53.4	56.2	64.2	69.3
1493D	13.6	43.4	53.5	58.3	58.0	58.0
1451D	7.6	38.7	53.1	52.2	54.0	54.0
1508D	4.8	17.2	15.9	17.4	20.4	22.8

The total volatiles yield data are shown in Fig. 1.8 as a function of the carbon to hydrogen ratio in the parent coal. The measured yields in the CDL and the CCL exceed the ASTM total volatiles yields for all five coals. The yields from the CDL-0 low rank coal experiments are 3-4% lower than the yields in the CCL-0 experiments, indicating that the increased temperature in the CCL resulted in additional mass release. However, for the Pittsburgh #8 hva bituminous coal (1451D) and the Pocahontas low volatile bituminous coal (1508D), the yield obtained in the CDL-0 experiments was nearly identical to the yield obtained in the CCL-0 experiments. The extent of mass release in the CCL-6 and CCL-12 experiments was 3 to 13% higher than in the CCL-0 experiment, with the most dramatic increase in yield with oxygen observed for the low rank coals. The increase in yield seen for the low rank coals is most likely due to the onset of heterogeneous char oxidation in the late stages of devolatilization. This hypothesis is consistent with the fact that lignite char reactivities are higher than bituminous coal char reactivities. The data for the low volatile coal (1508D) indicate that the presence of oxygen increases the extent of mass release at comparable residence times. The reactivity of high rank coals is much lower than the lignites, and hence chars from high rank coals shouldn't be expected to

react with oxygen during the late stages of devolatilization. For such high rank coals, the low volatiles flux may allow more oxygen penetration to the particle surface at early residence times, allowing more time for early char oxidation to occur than for the more volatile coals.

b. Swelling Behavior

The results of Lightman and Street (1968, 1969) indicate that particle swelling is reduced in the presence of oxygen. A possible physical explanation for this phenomenon is that oxygen scavenges the radicals in the coal particle as the particle begins to soften, forming a rigid structure before the onset of devolatilization drives the oxygen from the particle surface. As indicated above, the observed difference in swelling behavior between previous experiments in the CDL and CCL for Pittsburgh #8 hva bituminous coal particles may be caused by the difference in the gas phase oxygen concentration in the two experiments. Experiments were therefore performed in the CDL to determine the effect of ambient gas phase oxygen concentration on the swelling behavior of a Pittsburgh #8 hva bituminous coal (PSOC-1451D). Oxygen

Figure 1.8 Comparison of mass release due to devolatilization in different experiments in the CDL and CCL for five PSOC-D coals. The ASTM total volatiles yields are shown for reference. The elemental oxygen level in the parent coal is used as an indicator of coal rank.

was added in controlled amounts to both the flow reactor gas and the coal entrainment gas. Oxygen concentrations in the flow reactor were checked with an oxygen analyzer. Initial experiments were performed at low oxygen concentrations to reduce wear of flow reactor components and to limit the amount of char oxidation in the reactor. The apparent densities of the samples are an indicator of the amount of particle swelling, since the extent of mass release is virtually identical for all samples. For this coal, apparent density ratios of 0.2 correspond to 50% diameter change, while density ratios of 0.4 correspond to diameter changes of less than 10%.

The first set of samples were collected at the exit of the flow reactor (250 mm from the point of coal injection) in both the 1050 K and 1250 K gas conditions. Two general types of particles were encountered in the collected samples: (1) round, partially-transparent, balloon-like cenospheres; and (2) molten opaque particles with many blow holes. These two types of particles are illustrated in Fig. 1.9; the transparent nature of the particles is difficult to see in these photographs. The balloon-like cenospheres are much larger (110 to 180 μm) than the opaque particles (50 to 130 μm). Roughly 30-40% of the particles in a given sample were balloon-like cenospheres. The two types of particles were observed in earlier electron micrographs and cross section photographs (Fletcher and Hardesty, 1987; see also Lightman and Street, 1968), although the electron micrographs do not reveal the transparent nature of the balloon-like cenospheres. Cross-section photographs show large internal voids (30-50 μm in diameter) in most of the particles. The balloon-like cenospheres are much lighter (lower apparent density) than the opaque particles, and accumulate at the top of the sample vials. Initial tap density measurements were performed on only a portion of the collected samples; the densities from these experiments were skewed because the balloon-like cenospheres were located at the top of the sample vial. This may be a source of error in previously reported experiments. Care was taken to use all of the sample from a given experiment during the tap density measurements reported here in order to avoid density classification.

Results of the sampling experiments conducted in the 1250 K gas condition in the CDL for PSOC-1451D (63-75 μm) are shown in Fig. 1.10. Samples were obtained at an axial distance of 250 mm, corresponding to residence times of 250 ms. Particle ignition was not observed in these experiments. The data indicate that the apparent density of the particles begins to rise at an ambient oxygen concentration of 3%. Optical microscopy of these samples showed, however, that the rise in apparent density is due to the partial oxidation and fragmentation of the balloon-like cenospheres. The apparent density of a broken shell fragment is much greater than that of an intact hollow sphere, since apparent density is the mass per external volume. The thin walls of balloon-like cenospheres burn more rapidly than the thick-walled cenospheres, and it is possible that the balloon-like cenospheres fragment due to oxidation prior to the first sampling location in most char combustion experiments. An examination of samples obtained in the char combustion experiments in the CCL revealed the absence of any transparent cenospheres; these types of particles were either not formed or were consumed upstream of the sampling location.

a. Balloon-like cenospheres from the top of the sample vial

b. Opaque particles from the bottom of the sample vial

Figure 1.9 Photographs of char particles from PSOC-1451D (63-75 μm initial size fraction) collected at 250 ms in the 1250 K gas condition in 3% oxygen in the CDL. Ten divisions on the size scale are equivalent to 139 μm .

Figure 1.10 Apparent density ratios (ρ/ρ_0) for char particles from PSOC-1451D (63-75 μm size fraction) collected at 250 ms in the 1250 K gas condition in the CDL at different gas phase oxygen concentrations.

Figure 1.11 Apparent density ratios (ρ/ρ_0) for char particles from PSOC-1451D (75-106 μm size fraction) collected at 130 ms in the 1250 K gas condition in the CDL at different gas phase oxygen concentrations.

A second set of experiments was performed in the CDL to determine the effect of gas phase oxygen concentration on the degree of swelling during pyrolysis before the onset of char oxidation. The 75-106 μm size fraction of PSOC-1451D Pittsburgh #8 hva bituminous coal was used for these experiments, due to limited quantities of the 63-75 and 106-125 size fractions. Fletcher (1989) showed that the main region of mass release for the 1250 K gas condition occurs at residence times between 70 and 100 ms. Samples were therefore collected at residence times of 130 ms to ensure completion of devolatilization and to minimize residence time for oxidation of the balloon-like cenospheres. Oxygen concentrations of 0, 5, and 10 mole-% were employed in these experiments. Ignited particles were observed in the 10% oxygen experiments, with ignition of a few particles starting at 90 ms; no particle ignition was observed in the 5% oxygen experiments. Particle luminosity ceased at the probe tip due to the helium quench jets. Balloon-like cenospheres were observed in samples from all three oxygen conditions, since any ignited particles were quenched within 10-40 ms. The apparent density ratios of samples obtained in the CDL are all on the order of 0.15, as shown in Fig. 1.11. From these experiments, it is concluded that the ambient oxygen concentration does not affect the particle swelling behavior during pyrolysis at heating conditions encountered in the CDL ($\sim 10^4$ K/s).

Pyrolysis experiments were conducted in the CCL at higher heating rates and temperatures by adjusting the flame stoichiometry to achieve post-flame oxygen levels in the 50 ppm range (referred to as 0% O_2). Mass release for this set of experiments are reported above in Table 1.3. The apparent density ratios (ρ/ρ_0) and the swelling ratios (d/d_0) obtained in the CDL and CCL for different coal types are given in Table 1.4. These data indicate that the oxygen concentration has little effect on the swelling behavior of coal particles sampled in the CCL (where heating rates are approximately 10^5 K/s). Pittsburgh #8 coal particles swell by approximately 50% in the CDL experiments in oxygen concentrations ranging from 0 to 10%, and the apparent density ratios range from 0.15 to 0.20. These same particles swell by less than 10% in the CCL, even in the 0% post-flame oxygen condition. The differences in particle swelling behavior observed in the two reactors is therefore attributable to (a) differences in particle heating rate, or (b) the presence of combustion products (H_2O , CO_2 , and radicals such as OH) from the flame in the CCL.

Table 1.4
Apparent Densities and Swelling Ratios for Chars Collected
in the CCL at Three Different Gas Phase Oxygen Concentrations

a. Results of CCL, 0% Oxygen Experiments (47 ms residence time)

PSOC-	Coal	Size Fraction (μm)	Apparent Density (ρ/ρ_0)	Mass Remaining (m/m_0)	Diameter Change (d/d_0)
1507	Beulah Zap	75-106	0.64	0.48	0.90
1445	New Mexico Blue	106-125	0.32	0.40	1.08
1493	Illinois No. 6	106-125	0.35	0.48	1.11
1451	Pittsburgh No. 8	63-75	0.39	0.50	1.08
1508	WV Pocahontas	106-125	0.57	0.86	1.14

b. Results of CCL, 6% Oxygen Experiments (47 ms residence time)

PSOC-	Coal	Size Fraction (μm)	Apparent Density (ρ/ρ_0)	Mass Remaining (m/m_0)	Diameter Change (d/d_0)
1507	Beulah Zap	106-125	0.61	0.47	0.92
1445	New Mexico Blue	106-125	0.46	0.49	1.02
1493	Illinois No. 6	106-125	0.52	0.49	0.97
1451	Pittsburgh No. 8	106-125	0.38	0.50	1.10
1508	WV Pocahontas	106-125	0.46	0.83	1.22

c. Results of CCL, 12% Oxygen Experiments (47 ms residence time)

PSOC-	Coal	Size Fraction (μm)	Apparent Density (ρ/ρ_0)	Mass Remaining (m/m_0)	Diameter Change (d/d_0)
1507	Beulah Zap	106-125	0.63	0.47	0.91
1445	New Mexico Blue	106-125	0.39	0.49	1.08
1493	Illinois No. 6	106-125	0.47	0.49	1.01
1451	Pittsburgh No. 8	106-125	0.39	0.50	1.08
1508	WV Pocahontas	106-125	0.51	0.81	1.17

Conclusions

Based on the results of the experiments conducted in the CDL and the CCL as a function of gas phase oxygen concentration, the following conclusions are reached:

1. The degree of swelling during coal pyrolysis at rapid heating conditions ($> 10^4$ K/s) is not affected by the gas phase oxygen concentration. Changes in particle swelling caused by the presence of oxygen reported in other experiments may be due to partial oxidation of char samples subsequent to pyrolysis.
2. Pittsburgh #8 coal particles increased in diameter by 50% in the CDL experiments and by less than 10% in the CCL experiments. Differences in swelling behavior were caused by differences in particle heating rate and/or the presence of post-flame combustion gases (e.g., CO_2 , H_2O , or trace radical species).
3. An examination of samples obtained in the char combustion experiments in the CCL revealed the absence of any transparent cenospheres; these types of particles were either not formed or were consumed upstream of the sampling location.

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The experiments in the CCL were conducted in collaboration with Dr. Reginald E. Mitchell; William Kent and Scott Ferko helped with sampling system modifications and collection of the char samples.

PLANS FOR NEXT QUARTER

During the next quarter, NMR analyses of char particles and condensed tar samples from the CDL for additional coals will be completed. Preliminary tests will be conducted to determine the feasibility of performing gas species analyses in the CDL with minor modifications. These tests include the use of Fourier Transform Infrared Spectroscopy (FTIR) with a 20 m path length cell. The results of the MS and NMR analyses

indicate the need for sampling of tars and chars at a new gas condition (1150 K) and at longer residence times in the 1050 K gas condition. An 1150 K gas condition will be characterized during the next quarter, and samples will be obtained for one coal at this condition and at longer residence times in the 1050 K gas condition. In addition, the development of the chemical percolation devolatilization (CPD) model will continue.

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U.S. DEPARTMENT OF ENERGY

MILESTONE SCHEDULE AND STATUS REPORT

1. Contract Identification		Task 1. Coal Devolatilization												2. Reporting Period 10/1/89 thru 9/30/90		3. Contract Number 0709	
4. Contractor (name, address)		Sandia National Laboratories Livermore, CA 94551-0969												5. Contract Start Date 10/1/89		6. Contract Completion Date Continuing	
7. Identification Number		8. Reporting Category (e.g., contract line item or work breakdown structure element)												9. Fiscal Year and Months		10. Percent Complete	
		Fiscal Year 1990															
		<div> <div> <div>OCT</div> <div>NOV</div> <div>DEC</div> <div>JAN</div> <div>FEB</div> <div>MAR</div> <div>APR</div> <div>MAY</div> <div>JUN</div> <div>JUL</div> <div>AUG</div> <div>SEP</div> </div> </div>												a) Planned		b) Actual	
Subtask 1.1		Pyrolysis Product Compositions Modifications to reactor and sampling system Modifications to optical system Chemical Structure NMR studies CPD model improvements Transition from Devolatilization to Combustion CDL studies CCL studies MFC study												Plans Temperature Threshold 1493 1507 High Temperature New NMR Data CO/CO ₂			
Subtask 1.2																	
Subtask 1.3																	
Reports																	
Monthly																	
Quarterly																	
11. Remarks																	
12. Signature of Contractor's Project Manager and Date														13. Signature of Government Technical Representative and Date			

PROJECT TITLE: COAL COMBUSTION SCIENCE

**TASK 2: THE RATES AND MECHANISMS OF
COAL CHAR COMBUSTION**

ORGANIZATION: Sandia National Laboratories, Livermore

CONTRACT NO.: FWP 0709

REPORTING PERIOD: April 1 - June 30, 1990

REPORTED BY: R. E. MITCHELL and D. R. HARDESTY

Phone: FTS 234-2449 and 234-2321

OBJECTIVE FOR TASK 2

The objective of this task is to characterize the physical and chemical processes involved during coal char combustion as a function of coal type, particle size and temperature, and gas temperature and composition. The experimental endeavor provides the data required to develop a predictive model of the char combustion process. Specific objectives are being met by conducting basic research in three subtask areas as follows:

Subtask 2.1 Determination of Apparent Char Particle Burning Rates

The apparent, or overall char-particle burning rate, q , can be expressed as:

$$q = k_s P_s^n \quad (2.1)$$

where k_s is the apparent surface chemical reaction rate coefficient and n is the apparent reaction order with respect to the oxygen partial pressure at the particle surface, P_s . The goal of this subtask is to determine the apparent reaction order and the Arrhenius parameters that describe k_s for the chars of selected U. S. coals. *In situ* measurements of the sizes, temperatures, and velocities of individual particles and off-line analyses for apparent densities and relative mass losses of partially reacted char samples extracted from controlled gaseous environments are used to meet this objective. An adsorption-desorption kinetic mechanism will also be considered in the analysis of the data. Such a mechanism has a more fundamental basis than the n -th order power-law expression given above and will allow accurate predictive capability over a wider range of combustion conditions than is possible with the power-law expression.

In addition, included in this subtask are experiments to investigate char formation effects on reactivity and the reactivity of chars near burnout.

Subtask 2.2 Determination of the Intrinsic Chemical Reactivity of Chars

The intrinsic reactivity, q_i , can be expressed as:

$$q_i = \eta k_{s,i} C_s^m \quad (2.2)$$

where η is the effectiveness factor, $k_{s,i}$ is the intrinsic chemical reaction rate constant, and m is the true reaction order with respect to the oxygen concentration at the particle surface, C_s . The objective of this subtask is to determine the true reaction order and the Arrhenius rate parameters that describe $k_{s,i}$. Analyses of partially reacted coal chars for specific surface areas, apparent densities, and porosities are required. Combined with size, temperature, and mass loss measurements, these properties allow the evaluation of the effectiveness factor, the true reaction order, and the Arrhenius rate parameters for $k_{s,i}$. Efforts in this subtask also include the development of an adequate rate expression and evaluation of rate constants for the intrinsic chemical reactivity when an adsorption-desorption reaction mechanism is employed.

Also included in this subtask is the investigation of the relation between chemical structure and reactivity for coal chars.

Subtask 2.3 Determination of Nitrogen and Sulfur Release Rates

The rates at which nitrogen and sulfur are released during char oxidation as a function of coal type will be determined. This requires determination of the elemental compositions of partially reacted coal chars. The sulfur release rates will be considered with reference to the forms of sulfur encountered in the parent coals.

The results of this project will provide a data base on the reactivities of the chars of selected U. S. coals and on the release rates of N and S from the char under typical pulverized-coal combustor conditions. The char oxidation models developed during the course of this investigation will be concise enough for use in coal flame simulation codes. The models will allow the accurate prediction of particle size, temperature, and mass during the char oxidation process.

SUMMARY OF TECHNICAL PROGRESS DURING THIS QUARTER

During this quarter, experiments aimed at determining whether the burning rates of coal chars depend upon the conditions under which the chars were formed were continued. Four coals, ranging in volatile matter content from 17% to 62%, are used in the study: Illinois #6 (PSOC-1493D), a hvB-bituminous coal; Blue #1 (PSOC-1445D), a subbituminous coal from New Mexico; Lower Wilcox (PSOC-1443D), a lignite from Texas; and Lower Kittanning (PSOC-1516D), a lv-bituminous coal from Pennsylvania. Three oxygen-level environments were used to produce the chars: an

almost oxygen-free environment (50 ppm oxygen), a 6 mole-% oxygen environment, and a 12 mole-% oxygen environment. Gas temperatures during devolatilization were nominally 1700 K.

The apparent densities of the coal chars produced under the different devolatilization conditions were measured. With the higher rank, lower volatile matter-containing coals, the apparent densities of the chars produced in the 50 ppm oxygen environment were greater than those produced in the 6 and 12 mole-% oxygen environments. This may be indicative of early oxidation, some of which could have occurred during the final stages of devolatilization. With the lower rank coals, the apparent densities of the char produced in the different oxygen level environments were essentially the same.

The chars will be further characterized to determine their specific surface areas and chemical properties. The chars will then be re-injected into the laminar flow reactor and *in situ* size, temperature, and velocity measurements will be made. The data will be used to determine overall particle burning rates. During this quarter, *in situ* measurements were obtained for the char particles of the Illinois #6 coal that were produced in the three different environments.

Also during this quarter, a model for the apparent density of a coal char particle that allows for the particle's mineral matter content was derived. The char particle is assumed to consist of two components: a combustible component whose apparent density changes with burnoff and a non-combustible component (the mineral matter) whose apparent density is constant. Such a model is deemed to be necessary to describe the changes in the apparent densities of particles having high ash contents. Data obtained with Lower Wilcox coal (PSOC-1443D), a high-ash coal, indicate that the char particle apparent density decreases with burnoff during the early to middle stages of burnoff but increases during the late to final stages of burnoff. The apparent density model that is presently used in data analysis (Mitchell, 1987a,b) is not capable of describing this behavior. It is expected that the apparent densities of the chars of all coals increase during the final stages of burnoff when the apparent density of the ash has a pronounced effect on the apparent density of the particle. Thus, such a two-component apparent density model is necessary if the mode of particle burning is to be described accurately during the early to final stages of burning.

In addition, the analysis of the combustion data obtained with Blue #1 coal (PSOC-1445D) was continued this quarter. Blue #1 coal has the lowest ash content (~4% ash on a dry basis) of all the coals studied. Correspondingly, the measured variations in char particle temperatures, a consequence of particle-to-particle variations in ash content, are the narrowest -- the effects of ash on the temperatures the char particles attain during burnoff are minimal. Narrow size and temperature distributions allow effects associated with particle emissivities to be examined. Variations in particle emissivities lead to variations in heat loss rates from particles via radiation, and hence, lead to variations in the apparent chemical reaction rate coefficients determined for particles of the same size and temperature. The *in situ* size and temperature measurements were therefore used to quantify the effects of particle emissivity on the

values determined for the kinetic parameters that describe the apparent chemical reaction rate coefficients. The results indicate that if the emissivities of char particles vary widely, the temperature dependence of the apparent chemical reaction rate coefficients may be incorrectly assessed unless different particle emissivity ranges are analyzed separately.

Specific highlights of this quarter's research activities are discussed below.

Subtask 2.1. Determination of Apparent Char Particle Burning Rates

Char Formation Effects

The coals employed in the investigation of char formation effects on overall particle burning rates are: Illinois #6 (PSOC-1493D), a hvB-bituminous coal; Blue #1 (PSOC-1445D), a subbituminous coal from New Mexico; Lower Wilcox (PSOC-1443D), a lignite from Texas; and Lower Kittanning (PSOC-1516D), a lv-bituminous coal from Pennsylvania. Particles in the 106 to 125 μm size-range were used. Table 2.1 gives pertinent information about each coal (as obtained from the Penn State Coal Data Base) that may influence the morphology of the particles formed during heat treatment. Huminite, the most uncommon of the maceral groups listed, is the petrographic name given to the maceral group that contains the precursors of vitrinite in the peat and brown-coal stages of vitrinite formation. For the younger, lower rank coals, the huminite content is given and for the older, higher rank coals, the vitrinite content is given, the huminite having evolved to vitrinite.

Table 2.1

Chemical Data of Coals Employed in the Study of Char Formation Effects

	Illinois #6 PSOC-1493	Blue #1 PSOC-1445	Lower Wilcox PSOC-1443	L. Kittanning PSOC-1516
<u>Prox. Analysis dry</u>				
%-Ash	15.17	4.6	21.43	10.31
%-Volatile Matter	37.91	45.95	61.81	17.73
%-Fixed Carbon	46.92	49.45	16.76	71.96
<u>Maceral Comp., dmmf</u>				
%-Huminite	- -	83.1	90.0	- -
%-Vitrinite	86.4	- -	- -	90.0
%-Inertinite	12.2	13.2	6.9	9.9
%-Liptinite	1.4	3.7	3.1	0.1

Lightman and Street (1968) and Street *et al.* (1969) noted that the higher the vitrinite content of a coal, the greater the degree of cenosphere formations during heatup and devolatilization. The cenospheres formed were thin-walled, some particles having a single cavity, others having as many as three or four. Noting the high vitrinite contents of the Illinois #6 and Lower Kittanning coals, such cenosphere formation is anticipated. Street *et al.* (1969) noted that lower rank coals formed thick-walled, lacy cenospheres with a larger number of smaller cavities. It is likely that huminite lacks the thermoplastic behavior of vitrinite. Thus, with the lower potential for swelling, it is expected that chars produced from low rank coals under different devolatilization conditions will not differ as much in morphology as chars produced from higher rank coals under similar devolatilization conditions.

Char samples were obtained by injecting the raw coals in flow reactor environments containing $\sim 5 \times 10^{-3}$ (50 ppm), 6, and 12 mole-% oxygen. Particles were extracted from the various environments at a height of 6.4 cm above the reactor inlet, at a particle residence time of about 47 ms. As evidenced by the disappearance of volatile clouds surrounding the devolatilizing coal particles in the 6 and 12 mole-% oxygen environments, particles were extracted just subsequent to devolatilization and volatiles combustion. During sample collection, tars and chars were separated using a cyclone installed into the solids sampling system.

The gas temperature profiles in each of the gaseous environments established in the flow reactor were nearly similar, the gas temperatures being nominally 1700 K during the region of particle heatup and devolatilization. Particle heating rates in the three environments were therefore, nearly similar. However, the peak heating rates the coal particles attained during devolatilization in the 6 and 12 mole-% oxygen environments may have been slightly higher than those in the 50 ppm oxygen environment due to the higher temperatures surrounding the particles as a consequence of volatiles combustion in the particles' boundary layers. Coal particle heating rates are estimated to be of the order 10^5 K/s.

The results of Lightman and Street (1968) and Street *et al.* (1969) indicate that coal particles treated in inert environments have more open structures and swell more than those treated in oxygen-containing environments, and that swelling is influenced by the temperature of the gaseous environment. Thus, due to the different oxygen-levels employed and the differences in gas temperatures in the vicinity of the particle surfaces owing to volatiles combustion, differences in the morphology of the chars produced are expected, especially with the bituminous coals.

For each of the chars produced, a value of m/m_0 at the extraction height was determined from the measurements of the weight of char collected (m) to the weight of coal fed (m_0). The values are considered to be preliminary, for they have not yet been confirmed by using Si, Al, or Ti as tracers. The bulk densities of the chars were determined by measuring the weights of beds of particles vibrated to minimum volumes. A void volume fraction of 0.42 (a value determined in previous tests by comparing bulk density measurements with mercury porosimetry measurements) was

Table 2.2

Fractional Mass Remaining and Apparent Density of the Chars Produced in Three Oxygen-level Environments. Initial Particle Size: 106-125 μm

	50 ppm O ₂ <u>Environment</u>	6% O ₂ <u>Environment</u>	12% O ₂ <u>Environment</u>
<u>Lower Wilcox Coal, PSOC-1443D</u>			
Fractional mass remaining, m/m_0	0.60	0.48	0.44
Apparent Density, g/cc	1.02	1.01	0.98
<u>Blue #1 Coal, PSOC-1445D</u>			
Fractional mass remaining, m/m_0	0.51	0.46	0.39
Apparent Density, g/cc	0.41	0.42	0.41
<u>Illinois #6 Coal, PSOC-1493D</u>			
Fractional mass remaining, m/m_0	0.55	0.52	0.47
Apparent Density, g/cc	0.55	0.50	0.50
<u>Lower Kittanning Coal, PSOC-1516D</u>			
Fractional mass remaining, m/m_0	0.80	0.77	0.76
Apparent Density, g/cc	0.86	0.69	0.68

used to obtain apparent densities. Table 2.2 gives the information obtained for the chars produced for each of the coals employed. The apparent densities of the chars of the lower rank Lower Wilcox and Blue #1 coals are nearly the same. This may be due to the huminite content of the coals, which causes the coals not to swell as much during heat treatment. With the higher rank Illinois #6 and Lower Kittanning coals, however, the apparent densities of the chars produced in the 50 ppm O₂ environment significantly differ from those produced in the 6 and 12 mole-% O₂ environments. This is no doubt due to the vitrinite content of the coals, which causes the particle to be sensitive to the conditions of heat treatment. Note that the m/m_0 values of the chars produced in the 50 ppm O₂ environment are greater than those produced in the 6 and 12 mole-% O₂ environments. This is indicative of early oxidation, some of which may have occurred during the final stages of devolatilization. Oxidation during the final stages of devolatilization is especially likely with coals having low volatile matter contents since the flux of volatiles from the particle's surface and the consumption of oxygen via volatiles combustion in the particle's boundary layer are not sufficient to prevent oxygen from reaching the particle. The apparent densities of the chars

produced in the 6 and 12 mole-% O₂ environments may be affected by early oxidation as well. Any effects of oxidation are expected to be minimal in the 50 ppm oxygen environment.

The chars produced will be further characterized to determine their specific surface areas and chemical properties. Ash analyses will be used to confirm the values of m/m_0 determined from the mass loss measurements. The chars will then be re-injected into the laminar flow reactor and *in situ* size, temperature, and velocity measurements will be made. The data will be used to determine overall particle burning rates. Any differences in the rates determined for the chars of the same coal should be attributable to the initial characteristics of the chars.

During this quarter, *in situ* measurements were obtained for the char particles of the PSOC-1493D coal that were produced in the three gaseous environments. Measurements were made at 6.4, 12.7, 19.1, and 25.4 cm above the reactor inlet. The measurements will be used to determine overall particle burning rates and the associated chemical reaction rate coefficients.

A Model for the Apparent Density of a Coal Char Particle

Data obtained with the high-ash coals indicate that the apparent density of the char decreases with burnoff during the early to middle stages of burnoff, but increases during the late to final stages of burnoff. Increases in the apparent densities of particles with mass loss are expected at high extents of burnoff for all coal chars as the apparent density of the ash in the particle is approached. The model for the apparent density of the particle that is currently being used in data analysis is not capable of describing this behavior. Therefore, a model for the apparent density of a coal char particle that accounts for the particle's ash content was derived. With respect to the apparent density of the particle, the char is assumed to consist of two components: a combustible component whose apparent density changes with burnoff and a non-combustible component whose apparent density is constant. The non-combustible component consist of mineral matter and ash in the particle. It is not necessary to distinguish between the two with regard to the apparent density model, for all that is important in the model is that the loss of non-combustible material from the particle during char burnoff is negligible. For the sake of brevity, the non-combustible component will simply be referred to as the ash.

The apparent density of the particle is defined as:

$$\rho_p = \frac{\text{total weight of particle}}{\text{volume of particle}} = \frac{w_c + w_a}{V_p} \quad (2.3)$$

Rewriting in terms of the apparent densities of the combustible material and the ash and the volumes they occupy yields:

$$\rho_p = \frac{w_c}{V_p} + \frac{w_a}{V_p} = \frac{v_c}{V_p} \frac{w_c}{v_c} + \frac{v_a}{V_p} \frac{w_a}{v_a} = \frac{v_c}{V_p} \rho_c + \frac{v_a}{V_p} \rho_a \quad (2.4)$$

The weights of combustible material and ash in the particle can be expressed as:

$$w_a = x_a V_p \rho_p = v_a \rho_a \quad (2.5)$$

and

$$w_c = (1 - x_a) V_p \rho_p = v_c \rho_c \quad (2.6)$$

Utilizing Eqs. (2.5) and (2.6) to eliminate v_a and v_c from Eq. (2.4) yields the following relation for the apparent density of the coal char particle:

$$\frac{1}{\rho_p} = \frac{x_a}{\rho_a} + \frac{(1 - x_a)}{\rho_c} \quad (2.7)$$

This equation gives the apparent density of the particle in terms of the apparent densities of the ash and combustible material and the fraction of ash in the char particle. Since the weight of ash in the particle is assumed to be unchanged during burnoff, the fraction of ash is readily calculable from the fraction of the initial mass remaining (m/m_0) and the weight fraction of ash in the raw coal (X_a) using the relation $x_a = X_a/(m/m_0)$. This expression is only approximate since it is possible for some of the ash to leave the particle via reaction or vaporization processes during burnoff or to be convected from the particle during devolatilization (Baxter and Mitchell, 1989; Baxter *et al.*, 1990). Such losses are important with coals having relatively high pyritic iron contents and with coals having a large fraction of atomically-dispersed ash components. Of the coals examined in this project, at heating rates of the order 10^5 K/s, typically less than 30% (and most of the time less than 15%) of the ash is lost from the particle during combustion. During the early to middle stages of burnoff when the particle is mostly combustible material, the error incurred in assuming negligible ash loss during combustion is small. The error increases as burnout is approached, but never becomes critical.

When the combustible material is completely consumed, x_a equals unity and from Eq. (2.7), the apparent density of the particle equals the apparent density of the ash. The apparent density of the ash is assumed to remain constant during burnoff. Apparent density measurements of solid samples extracted from the flow reactor at residence times longer than the time for complete burnout yield the apparent density of the ash.

The apparent density of the combustible material is assumed to vary with burnoff in accord with the following power-law expression:

$$\rho_c/\rho_{c,i} = (w_c/w_{c,i})^\alpha \quad (2.8)$$

where $w_{c,i}$ and $\rho_{c,i}$ are the weight and apparent density, respectively, of the combustible material in the initial char particle that is formed just subsequent to devolatilization, and α is a burning mode parameter having a value between zero and unity. For α equal to zero, the apparent density of the particle remains constant

during burnoff, the particle diameter progressively decreasing with mass loss. For α equal to unity, the apparent density of the particle progressively decreases with mass loss, the diameter of the particle remaining constant up until complete burnoff, at which time the diameter decreases to a value that is consistent with a spherical ash particle of weight $w_a (= X_a m_0)$ and apparent density ρ_a . Such a power-law expression relating apparent density and the mass of the combustible material has been used to correlate data obtained with ash-free Spherocarb particles (see Mitchell, 1987a and Waters et al., 1988a). A theoretical justification for the power-law relation has been given by Essenhigh (1988).

Figures 2.1a-d show measurements and calculations of apparent density as a function of burnoff for the chars of three coals, Lower Wilcox, a high-ash coal (PSOC-1443D, $X_a = 0.21$), whose apparent density starts to increase relatively early in burnoff (Fig. 2.1a), Hiawatha, a medium-ash coal (PSOC-1502D, $X_a = 0.09$), whose apparent density is relatively constant until late in burnoff (Fig. 2.1b), and Blue #1, a low-ash coal (PSOC-1445D, $X_a = 0.046$), whose apparent density decreases until late in burnoff before starting to increase to the apparent density of the ash at complete burnoff (Figs. 2.1c and 2.1d). Results are shown for two size ranges of the Blue #1 coal, 75 to 106 μm and 106 to 125 μm (as with the other coals). A value of 1.2 g/cc was used for the apparent density of the ash, as determined from the analysis of the char of Lower Wilcox coal at essentially 100% burnoff, daf. The factor $\rho_{c,i}/(w_{c,i})^\alpha$ that arises after rearranging Eq. (2.8) was evaluated from ρ_p and m/m_0 measurements obtained early in burnoff (at measurement heights of either 6.4 or 12.7 cm above the reactor inlet). For the chars of the Lower Wilcox and Hiawatha coals, $\alpha = 0.25$ best fits the data obtained in the 6 mole-% oxygen environment and $\alpha = 0.0$ best fits the data obtained in the 12 mole-% oxygen environment. A larger value for α in the lower O_2 -level environment is consistent with slower burning (and hence deeper oxygen penetration) in the lower O_2 -level environment. The near zero value for α for the char of Blue #1 coal (a low-ash coal) is in agreement with the value of 0.15 determined by Mitchell (1988a) using the previous apparent density model that did not account for the ash in the particle.

The particle apparent density model described above has been incorporated into the data reduction scheme used to determine rate parameters from the measurements. As before, the particles are assumed to be spherical, permitting the calculation of particle diameter from values obtained for particle mass and apparent density.

Effect of Emissivity on Apparent Chemical Reaction Rate Coefficients

The analysis of the combustion data obtained with Blue #1 coal (PSOC-1445D) was continued this quarter. As reported earlier (Mitchell, 1988a), for char particles in 6 and 12 mole-% oxygen in the gas temperature range 1750 to 1550 K, burning rates were near the diffusion-controlled limits rendering it impossible to obtain reliable information on the chemical reactivity of the char particles using average values of particle sizes and temperatures (as outlined in Mitchell, 1987b). However, owing to the variations in particle temperatures and burning rates as a consequence of particle-to-particle variations in ash contents, not all the particles were burning at the diffusion-limited rates. Thus, examination of individual particles (and not the average

Figure 2.1 Measured (points) and calculated (lines) particle apparent density as a function of burnoff for the chars of three coals: (a) Lower Wilcox coal, 106 to 125 μm initial particle size range, (b) Hiawatha coal, 106 to 125 μm initial particle size range, (c) Blue #1 coal, 75 to 106 μm initial particle size range, and (d) Blue #1 coal, 106 to 125 μm initial particle size ranges.

temperatures of particles that fall within ten-micron size bins, as outlined in Mitchell, 1987b) allows the determination of apparent chemical reaction rate coefficients.

Blue #1 has the lowest ash content (~4% ash on a dry basis) of all the coals studied. Correspondingly, the measured variations in char particle temperatures, a consequence of particle-to-particle variations in ash contents, are the narrowest (since the effects of ash on the temperatures the char particles attain during burnoff are minimal). Figure 2.2 shows the particle temperature distributions measured in the 6 and 12 mole-% oxygen environments. The distributions are noted to be quite narrow, until near burnout when the ash content of the particle has a significant affect on the particle temperature (Mitchell, 1990). The relatively narrow size and temperature distributions allow effects associated with particle emissivities to be examined. The *in situ* size, temperature, and velocity measurements were therefore used to quantify the effects of particle emissivity on the values determined for the apparent chemical reaction rate coefficients.

Pertinent information obtained from analysis of the char samples extracted from the flow reactor are presented in Table 2.3. Mass loss data may differ slightly from that previously presented (Mitchell, 1988a) since the values presented here are mean values, as determined from value of m/m_0 obtained using Si, Ti, Al, and total ash as tracers, as well as from the ratio of the weight of coal fed to the weight of char collected at the measurement height. The table also shows the average emissivities of char particles (calculated using the *in situ* size and temperature measurements and the particle's radiant intensity in Wien's approximation to Planck's Law), and the standard deviations in the emissivity distributions. A tungsten lamp was used to determine the system-dependent calibration constant of the particle-sizing pyrometer. For comparison, with ash-free spherical Spherocarb particles, average emissivities are 0.85 and standard deviations are about 0.1 at each measurement height when the same reactor gaseous environments are employed.

As has been remarked many times in the past, the calculated particle emissivities are only approximate. All errors incurred in determining the calibration constant or in determining the size and temperature of the char particle are reflected in the value determined for the emissivity. Non-sphericity effects are the dominate causes of error. Calculated particle emissivities are in the range 0.25 to 0.8. Low values may be associated with the mineral matter in the particle or they may be a consequence of non-spherical particles, where the larger dimension of the particle was measured. The data support char particle emissivities in the range of 0.55 to 0.65 during the early to relatively late stages of burnoff. As burnout is approached, the emissivity of the particle decreases to the emissivity of the ash in the particle. As suggested by the values determined from the measurement at 99% burnoff, daf, the ash of Blue #1 coal has an emissivity less than 0.5.

The *in situ* size, temperature, and velocity measurements of individual particles (Mitchell, 1988a) were combined with the m/m_0 and apparent density measurements to determined overall particle burning rates and apparent chemical reaction rate

Figure 2.2 Measured temperature distributions for Blue #1 coal char particles at various extents of burnoff in 6 and 12 mole-% oxygen environments

Table 2.3

**Burnoff and Apparent Density Measurements of the Chars of
Blue #1 Coal (initial particle size range, 106 - 125 μ m)**

6 mole-% Oxygen

Sampling height, cm	0.0	6.4	12.7	19.1	25.4
Approximate residence time, ms	0	47	72	95	117
Fractional mass remaining, m/m ₀	1.0	0.49	0.35	0.30	0.27
Fractional burnoff, daf	0.0	0.53	0.68	0.73	0.77
Apparent density, g/cc	1.12	0.35	0.34	0.32	0.29
Average particle emissivity, ϵ_p	---	---	0.53	0.60	0.60
Standard deviation in ϵ_p	---	---	0.13	0.09	0.08

12 mole-% Oxygen

Sampling height, cm	0.0	6.4	12.7	19.1	25.4
Approximate residence time, ms	0	47	72	95	117
Fractional mass remaining, m/m ₀	1.0	0.49	0.26	0.13	0.06
Fractional burnoff, daf	0.0	0.53	0.78	0.91	0.99
Apparent density, g/cc	1.12	0.35	0.32	0.30	0.55
Average particle emissivity, ϵ_p	---	---	0.65	0.59	0.48
Standard deviation in ϵ_p	---	---	0.06	0.05	0.05

coefficients for individual particles. The equations used to describe a burning char particle in a flow reactor environment have been previously presented (Mitchell, 1988b). In the analysis employed here, the particles are assumed to be in thermal equilibrium with the ambient gas and CO is assumed to be the sole heterogeneous reaction product. An apparent reaction order with respect to the oxygen partial pressure of 0.5 is also assumed. Since only comparative rate coefficients are of interest at the present time, these assumptions are of little consequence and do not influence the conclusions reached concerning the effects of particle emissivity on burning rates.

Figures 2.3 to 2.5 show apparent chemical reaction rate coefficients determined for particles having emissivities in three separate ranges: 0.6 to 0.8, 0.4 to 0.6, and 0.2 to 0.4. Of all the particles monitored, roughly 13% had emissivities in the 0.2 to 0.4 range, 38% in the 0.4 to 0.6 range, and 49% in the 0.6 to 0.8 range in each of the gaseous environments employed. The lines in the figures are least squares fits to the individual rate coefficients; standard deviations between the observed rate coefficients and those calculated from the least squares fit are about 15%. Based on the slopes of the lines for the separate emissivity ranges, the apparent activation energy of the heterogeneous char oxidation reaction is in the range 33 to 36 kcal/mole.

Figure 2.3 Apparent chemical reaction rate coefficients for Blue #1 coal char particles having emissivities in the range 0.6 to 0.8 burning in 12% oxygen.

Figure 2.4 Apparent chemical reaction rate coefficients for Blue #1 coal char particles having emissivities in the range 0.4 to 0.6 burning in 12% oxygen.

Figure 2.5 Apparent chemical reaction rate coefficients for Blue #1 coal char particles having emissivities in the range 0.2 to 0.4 burning in 12% oxygen.

Figure 2.6 shows a comparison of the fits to the rate coefficients. At any specified particle temperature in the range 1500 to 2000 K, particles having emissivities in the range 0.6 to 0.8 have chemical reaction rate coefficients about 1.7 times higher than particles having emissivities in the range 0.2 to 0.4. The higher emissivity range yields higher rate coefficients because the higher the particle emissivity, the greater the heat loss rates due to radiation and hence, the higher the overall burning rate needed to attain any specified particle temperature.

Figure 2.7 shows the least squares fit to the apparent chemical reaction rate coefficients when all the individual particles, irrespective of emissivity, are considered ($0.2 < \epsilon_p < 0.8$). The activation energy determined is 41.8 kcal/mole, but as indicated in Fig. 2.8, such an activation energy would yield predicted rate coefficients (and particle temperatures) that are too high if the actual particle emissivity is in the 0.2 to 0.4 range, and too low if the particle emissivity is in the 0.6 to 0.8 range. These results indicate that if the emissivities of char particles vary widely, the temperature dependence of the apparent chemical reaction rate coefficients may be incorrectly assessed unless different emissivity ranges are analyzed separately.

As already indicated, the observed variations in particle emissivities may be due to particles that were not sized correctly (a consequence of irregularly-shaped particles). If so, the average values of emissivity may be representative of the true particle emissivities at the various extents of burnoff examined. Figure 2.9 shows the apparent chemical reaction rate coefficients determined when the average values of emissivity (see Table 2.2) are used at the various measurement heights. Note that the scatter is considerably reduced by using the average emissivity values. An activation energy of 36.8 kcal/mole is obtained from the least squares fit to the individual rate coefficients, a value that is in agreement with the values indicated by analyses of the separate emissivity ranges. The standard deviation between the observed rate coefficients and those calculated from the least squares fit is 9% when average emissivity values are used in data analysis.

Errors in determining particle size are expected since not all particles are spherical. As indicated in earlier work in which the effects of non-sphericity on the particle-sizing technique were quantified (Waters, *et al.* 1988b), for coal chars, measured diameters ranging from 0.76 to 1.14 times the expected values are likely. Such errors in size would yield calculated particle emissivities ranging from 1.73 to 0.77 times the true values. (It is possible to determine the error in particle emissivity due to an error in size since in the expression used to calculate particle emissivity, the product $d_p^2 \epsilon_p$ is constant.) Based on the size range of coal particles used in the combustion tests (106 to 125 μm), most of the measured char particle diameters are in the expected range when account is made for the possibility of irregularly-shaped particles. This suggests that the observed variations in emissivity are possibly due to the effects of non-sphericity on the sizing technique and not necessarily due to true emissivity differences that may result from particle-to-particle variations in ash contents. Such inherent differences in particle emissivities are believed to exist, however.

Figure 2.6 Comparison of least squares fits to the apparent chemical reaction rate coefficients for Blue #1 coal char particles having emissivities in the ranges 0.6 to 0.8, 0.4 to 0.6, and 0.2 to 0.4.

Figure 2.7 Apparent chemical reaction rate coefficients for Blue #1 coal char particles having emissivities in the range 0.2 to 0.8 burning in 12% oxygen.

Figure 2.8 Comparison of least squares fits to the apparent chemical reaction rate coefficients for Blue #1 coal char particles having emissivities in the indicated ranges.

Figure 2.9 Apparent chemical reaction rate coefficients for Blue #1 coal char particles calculated using the average particle emissivity at each measurement height: 0.65 at 12.7 cm (78% burnoff, daf), 0.59 at 19.1 cm (91% burnoff, daf), and 0.48 at 25.4 cm (99% burnoff, daf).

This analysis demonstrates the importance of accurately assessing char particle emissivities when determining kinetic parameters that describe the apparent chemical reaction rate coefficients from particle size and temperature measurements. Variations in calculated particle emissivities can arise as a result of irregularly-shaped particles that are not accurately sized. Variations in particle emissivities are also expected as a consequence of inherent differences in the physical and chemical properties of the various particles. This study indicates that the analyses of separate emissivity ranges yield accurate determination of the apparent activation energy of the coal char oxidation reaction. Data analysis using average values of emissivities determined for char particles at various extents of burnoff are recommended, for the use of such average values yields kinetic parameters that accurately reflect the temperature dependence of the apparent reaction rate coefficients.

PLANS FOR NEXT QUARTER

During the next quarter, the analysis of the combustion data to determine kinetic parameters for the chars of the various coals tested will continue. As suggested by the analysis presented above, the average values of emissivities determined at various extents of burnoff will be employed. To assure that this approach yields an activation energy for the char oxidation reaction that is representative of all particles, separate emissivity ranges will be analyzed as well. In addition, *in situ* size, temperature, and velocity measurements using the chars that were produced under different devolatilization conditions will continue. The data will be used to determine to what extent the apparent burning rates of coal chars depend upon how the chars are produced. Also, the chemical analyses of the chars collected at various extents of burnoff will commence during the next quarter. Data analysis will yield the release rates of sulfur and nitrogen from the char during burnoff for the various coals examined.

Data packages containing all the data obtained in the various combustion tests for each of the coals examined are being compiled. To date the packages contain the *in situ* size, temperature, and velocity measurements and the m/m_0 and apparent density measurements at each sampling height in each of the gaseous environments employed. During the next quarter, the chemical analyses of the chars collected will be included. The completed packages will contain the results of data analyses as well.

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NOMENCLATURE FOR TASK 2 SECTION

A_a	apparent pre-exponential factor, $\text{gC cm}^{-2} \text{s}^{-1} \text{atm}^{-n}$
C_s	oxygen concentration at the particle surface, mole cm^{-3}
E_a	apparent activation energy, cal mole^{-1}
k_s	apparent chemical reaction rate coefficient, $\text{gC cm}^{-2} \text{s}^{-1} \text{atm}^{-n}$
$k_{s,i}$	intrinsic chemical reaction rate constant, $(\text{mole O}_2)^{(1-m)} (\text{cm}^3 \text{fluid})^m \text{s}^{-1} (\text{cm}^2 \text{surface})^{-1}$
m	true reaction order (Eq. (2.2) or mass of a coal char particle, g
m_0	mass of a raw coal particle, g
M_c	molecular weight of carbon, gC mole^{-1}
n	apparent reaction order
P_s	oxygen partial pressure at the particle surface, atm
q	overall particle burning rate per unit external surface area, $\text{gC cm}^{-2} \text{s}^{-1}$
q_i	intrinsic chemical reaction rate, $(\text{mole O}_2) \text{s}^{-1} (\text{cm}^2\text{-surface})^{-1}$
R	gas constant, $\text{cal mole}^{-1} \text{K}^{-1}$
T_p	particle temperature, K
v_a	volume of particle occupied by mineral matter or ash, cm^3
v_c	volume of particle occupied by combustible material, cm^3
V_p	volume of particle $(= \pi d_p^3/6)$, cm^3
w_a	weight of mineral matter or ash in a particle, g
w_c	weight of combustible material in a particle, g
x_a	weight fraction of mineral matter or ash in a coal char particle
X_a	weight fraction of ash in a raw coal particle

Greek

η	effectiveness factor: the ratio of the actual reaction rate to that which would occur if the entire particle were exposed to the same oxygen concentration and temperature as that existing at the outer surface of the particle
ρ_a	apparent density of ash in the particle, g cm^{-3}
ρ_c	apparent density of combustible material in the particle, g cm^{-3}
ρ_p	apparent density of the particle, g cm^{-3}

VISITING STUDENTS

On May 25, Ms. Nadine de Coteau, a beginning graduate student in the Mechanical Engineering Department at Stanford University, completed her visit to Sandia where she helped perform experiments in the coal char combustion laboratory. Her help was greatly appreciated.

On June 1, Mr Lucien Johnson, a junior at Howard University in Mechanical Engineering, began a two and one-half month visit to Sandia. He will help perform experiments in the coal char combustion laboratory.

U.S. DEPARTMENT OF ENERGY

MILESTONE SCHEDULE AND STATUS REPORT

1. Contract Identification		Task 2. Coal Char Combustion												2. Reporting Period 10/1/89 thru 9/30/90		3. Contract Number 0709																																																											
4. Contractor (name, address)		Sandia National Laboratories Livermore, CA 94551-0969														5. Contract Start Date 10/1/89																																																											
		Principal Investigator: R.E. Mitchell Project Manager: D.R. Hardesty														6. Contract Completion Date Continuing																																																											
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Subtask 2.1		<p>Apparent Burning Rates: n-th order, power-law kinetics</p> <p>Adsorption/Desorption kinetics</p> <p>Char Formation Studies</p> <p>Unburned Carbon Studies</p> <p>Experimental Data Packages</p> <p>Intrinsic Reactivities (N₂ - BET areas)</p> <p>Char Surface Area Study</p> <p>NMR Study</p> <p>Nitrogen and Sulfur Release</p> <p>Laboratory Shutdown for Installation of new Safety System (2-3 months)</p>																																																																									
		<p>CDL Char Collection 1493, 1445 In-situ CCL tests on char samples</p> <p>MFC Char Collection 1451, 1493, 1443, 1445, 1488 In-situ CCL tests on char particles near burnout</p> <p>Surface Area Measurements Analysis 1493, 1443, 1445, 1488 Analysis 1507, 1508, 1502</p> <p>Measurements, 1502 Analysis</p> <p>Char Collection 1493, 1445, 1443 Samples Analyzed Data Analysis</p> <p>1451, 1493, 1443, 1445 1488, 1507, 1508, 1502</p>																																																																									
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PROJECT TITLE: COAL COMBUSTION SCIENCE
TASK 3: THE FATE OF MINERAL MATTER
ORGANIZATION: Sandia National Laboratories, Livermore
CONTRACT: FWP 0709
REPORTING PERIOD: January 1, 1990 - March 31, 1990
REPORTED BY: L. L. Baxter and D. R. Hardesty
Phone: FTS 234-2862 and 234-2321

OBJECTIVE FOR TASK 3

The long-term objective of this task is to gain quantitative understanding of the rates and mechanisms of selected aspects of mineral matter evolution, transport and deposition under conditions relevant to pulverized coal combustion. These selected aspects of mineral matter evolution include: (1) release of inorganic material from coal particles during reactions of the organic and inorganic portions of the particle and by vaporization; (2) changes in mineral matter composition during combustion; (3) size distributions of flyash formed during coal combustion; and (4) deposition of mineral matter on surfaces. These aspects of mineral matter evolution will be studied as a function of coal and mineral type, total ash loading, rate of organic and inorganic reaction, local gas conditions, and time.

The focus of research during FY90 is on (i) the release of inorganic material during coal devolatilization, (ii) the evolution of particle and flyash size distributions, and (iii) theoretical and experimental studies of ash deposition. Three subtasks are defined to address these issues.

Subtask 3.1. Release of Inorganic Material During Coal Devolatilization and Char Oxidation

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. 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 3.2. The Evolution of Particle and Fly ash Size Distributions

The goal of this subtask is to determine the extent of char fragmentation during pulverized coal combustion. This is accomplished by measuring the particle size distributions of the char and flyash and relating these through a mathematical model. The model indicates the number of flyash particles generated per original char particle, both for the overall fuel and as a function of size. These results are collected as a function of coal rank and of ash loading.

Subtask 3.3. Theoretical and Experimental Studies of Ash Deposition

Theoretical and experimental investigations of ash deposition are being conducted to determine the elemental composition of deposits as a function of coal type boiler operating conditions, and location within a boiler. The effect of deposit formation on heat transfer efficiency through simulated boiler tubes and waterwalls is also being studied. The mechanisms of deposit formation are being combined into an engineering model that predicts elemental deposit composition.

SUMMARY OF TECHNICAL PROGRESS DURING THIS QUARTER

Subtask 3.1. Release of Inorganic Material During Coal Devolatilization and Char Oxidation

Release of Inorganic Material due to Organic Reactivity

Previously reported results [Baxter, 1990b-d; Baxter et al., 1990] have identified coal devolatilization as a factor in mineral matter release from coal. These studies were based on titanium loss from size-classified coal samples. One of the modes of occurrence of titanium in coal is as an organically complexed metal [Finkelman, 1980]. The limited number of available studies in this area indicate that 10 to 15 percent of the total mass of titanium typically occurs in this mode. Titanium is among the most refractory materials in coal and is not expected to be subject to vaporization. Therefore it was used as an indicator of mineral release induced by coal devolatilization.

Previous reports also discussed the possibility of the same release mechanism applying to atomically-dispersed material of all types. Specifically, this mechanism would be expected to influence the release of alkali and alkaline earth minerals. This quarter data have been reduced that support this hypothesis. A size-classified sample of a subbituminous Multifuel Combustor coal (Smith-Roland, PSOC-1520d) was used to demonstrate this trend. The ultimate, proximate, calorific value and ash chemistry analyses of this coal are presented in Tables 3.1 and 3.2.

Table 3.1
Proximate, Ultimate and Calorific Value Analyses for the Coal Used to
Determine the Extent of Alkali Earth and Alkaline Metal Loss During Coal
Devolatilization

Smith-Roland Subbituminous C Coal (PSOC1520d)				
106-125 μ m Size Fraction*				
Proximate Analysis (mass %)			Ultimate Analysis	
	As Received	Dry Basis	Dry Basis	
Volatile	40.13	54.74	Carbon	62.18
Fixed Carbon	24.10	32.88	Hydrogen	4.87
Ash	9.08	12.38	Oxygen	24.15
Moisture	26.69		Nitrogen	0.92
Calorific Values			Sulfur	1.605
Equil. Moist.	8326 Btu/lb		Ash	9.95
Dry	11291 Btu/lb		Total	103.675

*Proximate analysis and calorific values are based on whole coal analysis. These analyses are not yet available for this size fraction.

Table 3.2
Elemental Ash Composition (Expressed as Oxides) in the Raw Coal Samples
Used to Determine the Extent of Alkali Earth and Alkaline Metal Loss During
Coal Devolatilization.

Smith-Roland Subbituminous C Coal (PSOC1520d)			
106-125 μ m Size Fraction			
Elemental Ash Chemistry			
Oxide	Mass % of Coal	Oxide	Mass % of Coal
SiO ₂	2.01	CaO	1.78
Al ₂ O ₃	1.28	Na ₂ O	0.135
TiO ₂	0.079	K ₂ O	0.022
Fe ₂ O ₃	1.38	MgO	0.408

This coal contains reasonably high concentrations of calcium, sodium and magnesium, a common characteristic of coals from the Powder River Basin. The potassium levels are low, near the detection limits of the inductively coupled plasma/atomic absorption analytical technique used in this investigation. Therefore, we focus our attention on release of calcium, sodium, and magnesium.

Time resolved data obtained from the char combustion laboratory (CCL) illustrating the release of calcium, sodium, and magnesium during coal devolatilization and combustion are presented in Figures 3.1 and 3.2. These data are derived from samples collected from the flow reactor with gas environments containing overall oxygen levels of 6 and 12 mole %, respectively. Experimental and analytical techniques used to produce these data are similar to those discussed previously [Baxter and Mitchell, 1990; Baxter et al., 1990].

Figure 3.1 Mass of alkali and alkaline earth metals released during coal devolatilization and char oxidation in a gas environment of 6 mole percent oxygen. Peak particle temperatures are 1700 K and occur after 45 ms residence time. All data are normalized by initial mass of each element.

Chemical fractionation results for the same rank coal from the same field (Wyodak/Anderson) indicate that approximately 40 percent of the calcium, 70 percent of the magnesium, and 95 percent of the sodium in this coal are atomically dispersed, i.e., extractable with either water or ammonium acetate. These results are typical of other coals from the same basin [Steadman, 1990].

Figure 3.2 Mass of alkali and alkaline earth metals released from Smith-Roland coal during coal devolatilization and char oxidation in a gas environment of 12 mole percent oxygen. Peak particle temperatures are 1850 K and occur after 45 ms residence time. All data are normalized by initial mass of each element.

Our previous data indicate that roughly half of the atomically dispersed titanium in coal is released during coal devolatilization under these experimental conditions, with the percentage increasing to roughly 100 percent as the rate of devolatilization increases [Baxter et al., 1990]. Similar trends are seen in Figure 3.1. About half of the atomically dispersed calcium, sodium and magnesium is released during devolatilization, with the subsequent release of more material during char oxidation. Replicate experiments were performed at particle residence times of 47 and 117 ms, and the 95 % confidence intervals for the data at these residence times are ± 0.05 and 0.03 , respectively. (No replicate experiments were performed at the intermediate particle residence times.) This indicates that between 70 and 90 percent of the total amount of alkali and alkaline earth material released from the coal particles is released during coal devolatilization in these experiments.

The particle temperatures are too low during particle heat up and devolatilization to allow significant vaporization of materials such as calcium and titanium occurring in mineral forms common to coal. Magnesium and sodium are more volatile in some mineral forms and could vaporize at lower temperatures than either calcium or tita-

nium. The data indicate that approximately the same fraction of the atomically dispersed material is released during coal devolatilization regardless of the chemical composition or volatility (in terms of relative vapor pressures) of the material. These trends support the hypothesis that mineral matter release by convective transport of coal volatiles contributes substantially to the release of atomically dispersed mineral constituents.

Figure 3.2 illustrates preliminary data collected from a gas environment containing 12 mole percent oxygen. None of the experiments summarized in this figure has been repeated and the confidence intervals are therefore quite large (approximately ± 0.4 , 0.15, and 0.15 at 47, 72, and 95 ms, respectively, for each species). Overall particle mass loss at 95 ms residence time is approximately 92 percent, including 97 percent loss of the organic matter and about 50 percent loss of the total ash. The same qualitative trend illustrated in Figure 3.1 is seen in Figure 3.2. Statistical confidence intervals associated with the data in Figure 3.2 are too large (due to a lack of replicated data) to distinguish between actual differences and experimental error.

Investigations of this mechanism of mineral matter release from coal in the Multifuel Combustor (MFC) are underway for a wide range of coals (see Table 3.5). These will be reported in the future.

Release of Iron-Containing Species due to Inorganic Reactivity

Experiments in our laboratory indicate a substantial loss of iron from pyrite in coal due to its thermal instability and reactivity to oxygen. Our hypothesized mechanism for this release has been previously reported [Baxter, 1990c-d; Baxter, 1989] and its salient features are summarized here. Figure 3.3 is a schematic representation of our hypothesized mechanism used to aid in this discussion.

The iron release mechanism is believed to be related only to coals containing iron in the form of pyrite. Pyrite is a common form of iron in US coals, particularly bituminous coals from the eastern US. The first particle shown in Figure 3.3 illustrates a typical particle of such coal after pulverization. The particle consists largely of coal, illustrated in black, with an included pyrite grain, illustrated in gray. In the figure, the size of the grain is exaggerated to aid in illustration.

Figure 3.3 Schematic representation of an iron release mechanism believed to be responsible for production of an iron fume from pyrite-bearing coal particles.

As the particle heats up and the coal devolatilizes, the pyrite particle undergoes a thermal decomposition reaction in which it loses slightly less than half of its original sulfur and forms a pyrrhotite complex with a stoichiometric formula of approximately

Fe₇S₈. This highly porous pyrrhotite grain is composed of small nodules approximately 0.1-0.7 μm in diameter, loosely linked by thin bridges. It is illustrated as a cluster of small spheres in the figure. Scanning electron micrographs (SEMs) of coal particles sampled from the CCL immediately after coal devolatilization (47 ms particle residence time with 106-125 μm particles) were previously reported [Baxter, 1990c-d; Baxter, 1989] and verify the porous nature of the pyrrhotite and the size of the nodules. All of the iron originally in the pyrite grain remains in the pyrrhotite grain at this stage of combustion. Both pyrite and pyrrhotite are reactive to oxygen, with kinetic rates of the same order of magnitude as coal char oxidation. However, the volatile cloud from the coal particles consumes local oxygen during coal devolatilization, as illustrated in the figure. Our data indicate little if any formation of iron fume at this stage of combustion. The pyrite grains also fracture during this stage [Baxter, 1990b], although only about 3 fragments form per grain, leaving relatively large fragments. The possibility of some of these fragments being released from the coal particle during this process is also illustrated in the figure.

The porous pyrrhotite grain is exposed to oxygen as the volatile cloud is swept away from the surface, as illustrated by the third particle in Figure 3.3. The porous structure disintegrates upon reaction with oxygen, producing a large number of small particles, as illustrated by the last particle in Figure 3.3. Some fraction of these small particles adhere to the char surface and some are convected away from the particle, assisted by the net outgassing of the char associated with oxidation and residual volatile release. SEMs collected in the CCL at this stage of combustion (72 ms residence time with 106-125 μm particles) were previously reported and illustrate the residual disintegrated structure of the pyrrhotite grain, and small iron-rich particles littering the neighboring regions of the coal particle. SEMs of fume samples collected at this stage of combustion in the CCL indicate a large number of iron-rich, small particulate with essentially no other refractory component in the fume. If exposure to oxygen is delayed until after the pyrrhotite grain melts ($\approx 1350\text{ K}$), little fume formation would be expected.

The dependencies of this fume formation mechanism on pyritic iron, as opposed to other modes of iron occurrence in coal, and on oxygen interactions with porous pyrrhotite grains indicates several expected qualitative trends in the data. For example, the mechanism predicts that the proportion of iron in the particle that is converted to fume decreases with decreasing ratio of pyritic iron to total iron in the coal. This mechanism predicts that iron fume formation is entirely eliminated if oxygen is eliminated from the carrier gas. Finally, if the exposure of pyrrhotite grains to oxygen is inhibited, either by being near the center of a large char particle or by being coated with a sulfate or oxidized layer, the amount of fume produced would be less than that produced from the same grains in the absence of oxygen inhibition.

Essentially all of these trends were documented in earlier reports. However, most of the previously reported results have focused on Illinois #6 coal (PSOC-1493d). Reasonably exhaustive studies of iron release from this coal were reported as a

function of oxygen penetration into the coal particle, oxygen level in the bulk gas, devolatilization rate, etc. [Baxter, 1990 c-d; Baxter and Mitchell, 1990].

Similar data on many additional coals were compiled this quarter and are summarized below. In most cases fewer experiments were repeated with these coals than with the Illinois #6 samples. The results of the iron release experiments are summarized in Figure 3.4 for 10 different coals. The majority of the coals are size-classified PSOC samples that were ground and stored under nitrogen. The corresponding coal and PSOC designations are summarized in Table 3.3. In most cases, the fractional loss of iron is a 'typical' result in the sense that several experiments were conducted with various particle sizes, oxygen concentrations, etc. The extent of iron loss is sensitive to each of these parameters. The ranks of the coals reported in Table 3.3 are based on DOE-supplied analyses of the whole coal [Goldberg, 1989]. No calorific value, forms of iron, or proximate analyses were performed for the size-classified samples used to generate the data shown in Figure 3.4, and therefore ranking and fractions of pyritic iron have not been determined specifically for these samples.

Figure 3.4 Typical amounts of iron mass released shortly after coal devolatilization and before substantial char oxidation. All amounts are normalized to original amounts in the coal.

Table 3.3
Coal Name, Rank, and PSOC Number for Coals Used in
Iron Evolution Experiments

Coal	Rank	PSOC Number
Lower Kittaning	lv Bituminous	1516D
Pocahontas #3	lv Bituminous	1508D
Pittsburgh #8	hva Bituminous	1451D
Illinois #6	hvb Bituminous	1493D
Kentucky #9		
Run of Mine	hvb Bituminous	—
Medium Cleaned	hvb Bituminous	—
Hiawatha	hvc Bituminous	1502D
Blue #1	hvc Bituminous	1445D
Lower Wilcox	Subbituminous C	1443D
Beulah Lignite	Lignite	1507D

Also included in the figure are the results from experiments with Illinois #6 and Kentucky #9 coals conducted in nitrogen to test the sensitivity of iron loss to the presence of oxygen. Additional experiments have been conducted with Dietz and Smith-Roland coals (PSOC-1488D and PSOC-1520D, respectively,) both from the Powder River Basin. Only two samples of the raw coal were analyzed for iron content in both cases, and the sample-to-sample variations of iron are too large to justify meaningful conclusions. Consequentially, these results will be reported in the future when better statistical information is available.

Three trends are seen in the data as a whole, all of which support the hypothesis that the chemical reactivity of the iron in the coal plays a major role in its release consistent with the mechanism illustrated in Figure 3.3. The first trend is a large sensitivity to the presence of oxygen in the environment. This is seen by comparing the results of experiments with the Illinois #6 and Pittsburgh #8 coals in environments containing oxygen (on the right) to those in inert (N₂) environments (on the left). The fractional loss of iron drops to within experimental error in cases where oxygen is eliminated from otherwise very similar experiments. This supports the hypothesis that reactivity to oxygen plays a major role in the release of iron.

The second trend is a sensitivity to exposure of the of the mineral grains to oxygen, even in environments with similar overall oxygen levels. The data to the right of the figure include coals that either (a) contain high levels of ash (≈ 30 percent for the Lower Kittaning coal) with presumably high amounts of excluded mineral grains, or (b) form cenospheres, thus concentrating existing mineral grains near the particle surface. Chars from low rank coals, which include Blue #1, Lower Wilcox, and Beulah, do not form cenospheres. Therefore the amount of mineral matter close enough to the char surface to be exposed to oxygen is smaller. This is one reason that these chars generally produced less iron fume. Specific experiments indicating

the same sensitivity by varying the depth of oxygen penetration in the char particles were previously reported.

The third trend is a sensitivity of the results to the presence of pyritic iron, as opposed to other forms of iron. The fractions of pyritic iron in low-rank coals typically is lower than that in eastern bituminous coals, with the possible exception of the Beulah lignite. The mechanism of iron fume formation illustrated in Figure 3.3 indicates that this is one explanation for the generally lower iron fume formation seen in the lower rank coals summarized in Figure 3.4. Note that the Blue #1 coal comes is most commonly reported as a subbituminous coal, although the analyses provided by DOE for PSOC-1445D indicate that this particular sample is a hvc bituminous coal.

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 [1982], in which iron enrichment was observed in much the same pattern as a function of coal rank as illustrated in Figure 3.3. Enrichment of iron in the submicron fume compared to the bulk coal greatly exceeded that of silicon, even though silicon is a less refractory species in essentially all of its forms. Similar results are reported by other investigators for a narrower range of coals. Most of the other species observed in the fume could satisfactorily ascribed 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. This quarter, we have identified a possible explanation for the differences in the amount of iron released as a fume between these several investigations. That 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 3.5 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. Our hypothesis is that the surface of the pyrite grains is rapidly oxidizing and producing a sulfated layer. This sulfate layer protects the pyrite grain from further oxidation.

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 Figure 3.5 are based is reasonably similar, with the important exception of overall iron content, to the size-classified Illinois #6 coal (PSOC-1493d) shown in Figure 3.4. The former was selected as the test fuel for these experiments. The ash compositions of these two coals are indicated in Tables 3.4 and 3.5. No formation of the iron fume was detected, in stark contrast to experiments previously reported which used the unweathered coal, as illustrated in Figure 3.6.

Figure 3.5 Decrease in pyritic iron content with exposure of pulverized coal to air at room temperature for approximately one week for three coals.

Table 3.4
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 3.5
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 3.6 Comparison of the fractional release of iron as a fume from a raw coal (see Table 3.5) and a weathered sample of similar coal (see Table 3.4). Data for the raw coal are from the char combustion laboratory. Data for the weathered coal are from the Multifuel Combustor.

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 char combustion laboratory using the size-classified samples of Illinois #6 coal and will be reported in future.

Subtask 3.2. The Evolution of Particle and Fly ash Size Distributions and Subtask 3.3. Theoretical and Experimental Studies of Ash Deposition

Progress during this quarter on these two subtasks is closely related and is therefore reported jointly.

A series of tests in the Multifuel Combustor are being performed with substantial support from Consolidation Coal Company (Consol). During this quarter, Robert Douglas, Murray Abbott, and Dee Reese, (all from Consol) have helped plan the test matrix and identify the coals. Testing of coals is underway. Contributions of Consol in this collaborative effort include (1) procurement and preparation of coals not already available at Sandia, (2) analysis of coal, fly ash and deposits, and (3) assistance in conducting tests in the MFC and in interpretation of results. Sandia's contributions include (1) major responsibility for testing coals in the MFC, including use of in situ diagnostics, (2) demonstration of and instruction in the use of ADLVIC as a predictive technique for ash deposit chemistry, (3) documentation of results. The investigators from Consol will continue to visit Sandia in the next quarter to help conduct experiments and to learn to use the ADLVIC deposition model. The data being collected relate to both subtasks 3.2 and 3.3.

Fifteen coals are being tested. The tests to be performed include (1) particle fragmentation measurements using the PCSV, (2) photography of ash deposition as a function of time, (3) collection of ash deposits on air-cooled targets simulating water walls and convective pass heat exchange tubes, and (4) characterization of changes in heat transfer efficiency with ash deposition. Each test includes a three hour deposition experiment. Each of these tests are being performed at three simulated boiler locations for each coal. A total of 45 experiments on fly ash formation and ash deposition are being conducted as a function of coal type, operating conditions, and location within a boiler.

The coals to be used in this study include representatives from most major US coal basins and blends of coals currently being used in utility boilers. Table 3.6 summarizes the coals to be used. Included in this list are all seven of the coals previously supplied by PSI and an additional eight coals selected and supplied in collaboration with Consol. Indicated ranks are based on analyses of the fuels as fired in the MFC and in some cases differ from traditional rank. Most notably, the Texas 'lignite' fired in the MFC is actually a subbituminous C coal according to ASTM ranking procedures. The Utah coal has not yet been received or analyzed. Coal analyses were provided by Bryers for the PSI coals [Boni et al., 1990] and replicated by Consol. The remaining coals were analyzed by Consol. The blends are ranked according to the properties of the blend and not those of the individual coals in the blend.

Table 3.6
Summary of the 15 Coals and Blends of Coals, Including Ranks, Used in Support
of Subtasks 3.2 and .3

Fuels Selected for Fly Ash Formation and Ash Deposition Experiments in the Multifuel Combustor			
Coal or Blend	Rank	Coal or Blend	Rank
Pittsburgh Seam	hvA Bituminous	Kentucky #9	hvC Bituminous
Pittsburgh #8	hvA Bituminous	Utah Blind Canyon	N/A
Eastern Blend	hvA Bituminous	Decker	hvC Bituminous
Upper Freeport	hvA Bituminous	Wyodak	Subbituminous B
Eastern Kentucky	hvA Bituminous	Eagle Butte	Subbituminous C
Pitt/Decker Blend	hvA Bituminous	Texas Lignite	Subbituminous C
Kentucky #11	hvB Bituminous	Beulah Lignite	Lignite A
Illinois #6	hvC Bituminous		

Experiments are being conducted, as described under subtask 3.2, to provide heat transfer, elemental composition, and other baseline data for this subtask. Progress in this area will be reported as results from these tests become available.

PLANS FOR NEXT QUARTER

During the next quarter experiments will be completed to determine mineral matter evolution from the matrix of test coals in the Multifuel Combustor. Experiments in the MFC will also be extended to examine the effect of weathering of the raw coal on the release of iron fume during combustion, and to provide additional data for and validation of the Sandia ADLVIC model.

REFERENCES FOR TASK 3 SECTION

- Baxter, L.L., "Evolution of Inorganic Material during Coal Devolatilization," Proceedings of the ASME Research Committee on Corrosion and Deposits from Combustion Gases Seminar on Fireside Fouling Problems, Provo, Utah, April 4-6, 1990a.
- Baxter, L.L., "Evolution of Mineral Grain Size Distribution During the Early Stages of Pulverized Coal Combustion," to appear in *Progress in Energy and Combustion Science*, 1990b.

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- Baxter, L.L., and R.E. Mitchell, "The Release of Iron During the Combustion of Illinois #6 Coal," submitted to Combustion and Flame, 1990.
- Baxter, L.L., R.E. Mitchell, and T.H. Fletcher, "Experimental Determination of Mineral Matter Release During Coal Devolatilization," presented at the Seventh Annual International Pittsburgh Coal Conference, Pittsburgh PA, September 10-14, 1990.
- Boni, A.A., Beér, J.M., Bryers, R.W., Flagan, R.C., Helble, J.J., Huffman, G.P., Huggins, F.E., Peterson, T.W., Sarofim, A.F., Srinivasachar, S., and Wendt, J.O.L., "Transformations of Inorganic Coal Constituents in Combustion Systems," Phase I Draft Final Report, U.S. DOE Contract No. CE-AC22-86PC90751, March, 1990.
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PUBLICATIONS, PAPERS AND PRESENTATIONS

The following papers and presentations were completed this quarter:

Baxter, L.L., "Evolution of Inorganic Material during Coal Devolatilization," *Proceedings of the ASME Research Committee on Corrosion and Deposits from Combustion Gases; Seminar on Fireside Fouling Problems*, Provo, Utah, April 4-6, 1990.

Baxter, L.L., "Experimental and Theoretical Investigations of Elemental Compositions of Ash," *Proceedings of the ASME Research Committee on Corrosion and Deposits from Combustion Gases; Seminar on Fireside Fouling Problems*, Provo, Utah, April 4-6, 1990.

Baxter, L.L., R.E. Mitchell, and T.H. Fletcher, "Experimental Determination of Mineral Matter Release During Coal Devolatilization," presented at the Seventh Annual International Pittsburgh Coal Conference, Pittsburgh PA, September 10-14, 1990.

Baxter, L.L., and R.E. Mitchell, "The Release of Iron During the Combustion of Illinois #6 Coal," submitted to *Combustion and Flame*, 1990

U.S. DEPARTMENT OF ENERGY

MILESTONE SCHEDULE AND STATUS REPORT

1. Contract Identification		Task 3. Fate of Mineral Matter		2. Reporting Period 10/1/89 thru 9/30/90		3. Contract Number 0709								
4. Contractor (name, address): Sandia National Laboratories Livermore, CA 94551-0969		Principal Investigator: L.L. Baxier Project Manager: D.R. Hardesty		5. Contract Start Date 10/1/89		6. Contract Completion Date Continuing								
7. Identification Number	8. Reporting Category (e.g., contract line item or work breakdown structure element)	9. Fiscal Years and Months Fiscal Year 1990												
		OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	10. Percent Complete a) Planned b) Actual
Subtask 3.1	Effect of Organic Reactivity on the Release of Inorganic Matter	Preliminary MFC tests and analysis of CCL and CCL data												
		Pyrite Oxidation: Effect on Furnace Formation												
Subtask 3.2	Evolution of Flyash Size Distribution	Completion of Data on PSI coals (Ken. #9, Ill. #6, Beulah lg.)												
		Studies on additional coals												
Subtask 3.3	Theoretical and Experimental Studies of Ash Deposition	Theoretical Ash Deposition Model												
		Deposition Experiments in MFC (some with Control)												
Reports														
	Monthly	▼	▼	▼	▼	▼	▼	▼	▼	▼	▼	▼	▼	▼
	Quarterly	▲		▲		▲		▲		▲		▲		▲
11. Remarks														
12. Signature of Contractor's Project Manager and Date														
13. Signature of Government Technical Representative and Date														

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