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Coal Combustion Science Quarterly Progress Report April - June 1994

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT

APRIL - JUNE 1994

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Submitted To: Philip Goldberg
Pittsburgh Energy Technology Center

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

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT — APRIL - JUNE 1994

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This document is a quarterly status report of the Coal Combustion Science Project that is being conducted at the Combustion Research Facility, Sandia National Laboratories, Livermore, California. The information reported is for the period April - June 1994.

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

Specific tasks include:

Task 1: Kinetics and Mechanisms of Pulverized Coal Char Combustion

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

The principal investigator on this task is Robert H. Hurt.

Task 2: Deposit Growth and Property Development in Coal-Fired Furnaces

The objectives of this task are to provide a self-consistent database of simultaneously measured, time-resolved, ash deposit properties in well-controlled and well-defined environments and to provide analytical expressions that relate deposit composition and structure to deposit properties of immediate relevance to PETC's Combustion 2000 program. The task includes the development and use of diagnostics to monitor, *in situ* and in real time, deposit properties, including information on both the structure and composition of the deposits.

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

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L.L. Baxter and D. R. Hardesty

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COAL COMBUSTION SCIENCE

QUARTERLY PROGRESS REPORT APRIL — JUNE 1994

EXECUTIVE SUMMARY

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

Work this quarter focused on our efforts to define the kinetics of heterogeneous fuel particle populations and on the role of particle structure in the char formation process. Our efforts culminated this quarter in the development of a combustion kinetic model for heterogeneous solid fuels. To provide data for the heterogeneity model, captive particle imaging (CPI) experiments were conducted on a series of coals of various rank to elucidate the relationships between reactivity, ash content, and swelling behavior. Experiments were carried out on a high rank coal, Pocahontas #3, PSOC-1508D, and on two low-rank coals, Beulah lignite, PSOC-1507D, and Dietz sub bituminous, PSOC-1488D. These experiments also represent the first application of the captive particle technique to raw coals, rather than prepared chars.

In addition, during the quarter, high resolution transmission microscopy fringe images were obtained of a series of partially combusted chars from the high rank Pocahontas #3 coal to examine the effect of rank on the dynamics of char carbon crystalline rearrangements.

Finally, during this quarter, development of the heated-wall reactor system continued. The reactor was used to generate partially-reacted samples of four coals from the PETC suite.

Task 2: Deposit Growth and Property Development in Coal-Fired Furnaces

During this quarter, tunable diode laser characterizations were completed under a broad range of conditions (laser current and diode temperature). These characterizations are used to determine operating parameters to be used when measuring spectra of alkali-containing vapors in Sandia's Multifuel Combustor. The laser was installed, aligned, and characterized using the FTIR spectrometer under a total of over 40 conditions. Strong multimode emission characteristics were noted, as was expected. The lowest wavenumber emission observed is located at about 387 cm^{-1} , near the NaCl bandhead, which is of great interest in the experiments to be conducted in the future. The hydroxide bands of sodium and potassium should be located at higher wavenumbers, more easily accessible by the laser. KCl bands are located at lower wavenumbers, clearly inaccessible by this diode.

Also during this quarter, high resolution spectra of the chlorides were collected (in collaboration with Prof. Peter Bernath, University of Waterloo, Canada) using high-resolution FTIR spectroscopy and a high temperature gas cell. These are used to determine the spectral regions to be investigated by TDL in future experiments. High-resolution, high-temperature spectra of

interfering species (principally water) were also collected to help identify the most appropriate spectroscopic regions.

In addition, this during the quarter, development of diagnostics for measuring deposit thickness *in situ*, in real time, nondestructively, and in realistic combustion environments was also made. This diagnostic is nearly completed and will become a routine part of the MFC measurements for ash deposition.

Finally, the effects of particle size and porosity on surface emissivity were illustrated this quarter and progress in describing these effects mathematically was made. The height, width, and shape of emission (or reflection) features from particulate samples can be affected by both particle size and bed porosity in such measurements.

Future Work

On the char combustion task, during the next quarter, particle density distributions will be incorporated into the heterogeneity submodel. This will complete the planned work under Subtask 1.1, aimed at defining the kinetics of heterogeneous fuel particle populations. Also during the next quarter, captive particle imaging results will be analyzed to compare extinction behavior at high conversion for coals of various rank. This will complete our planned work on Subtask 2.3, which is aimed at defining the role of particle structure on the char formation process. Finally, the first formulation of a char deactivation model will be attempted next quarter and more long residence time, high-conversion data will be taken in the heated-wall reactor system.

On the ash deposition task, during the next quarter, TDL experiments will continue to be conducted in the MFC in pursuit of chlorides and hydroxides of sodium and potassium. To assist in this investigation, Professor Peter Bernath of the Department of Chemistry at the University of Waterloo will spend the month of July at Sandia. Dr. Bernath is an internationally recognized expert in chemical spectroscopy. Model compounds (pure chlorides or hydroxides) will be used for the initial tests. Latter tests will use commercially significant US coals with reasonably high alkali concentrations (e.g. Powder River Basin Coals). Also, the laser-based deposit thickness measurement diagnostic and the dynamic deposit weight diagnostic will be further developed. During August, Scott Siquefield, a graduate student in the Department of Chemical Engineering, Oregon State University, will arrive to begin a one-year internship at Sandia. Scott is a member of Jim Frederick's group at OSU and will be working on a variety of projects related to ash behavior in coal and biomass combustion.

Also during the next quarter, the annual PETC contractor's review meeting is also scheduled and presentations summarizing our char combustion and ash deposition-related work will be delivered at this conference.

PROJECT TITLE: COAL COMBUSTION SCIENCE
TASK 1: KINETICS AND MECHANISMS OF
PULVERIZED COAL CHAR COMBUSTION
ORGANIZATION: Sandia National Laboratories, Livermore
CONTRACT: FWP 0709
REPORTING PERIOD: April 1 - June 30, 1994
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OBJECTIVE FOR TASK 1

The objective of Task 1 is to characterize the combustion behavior of selected U.S. coals under conditions relevant to industrial pulverized coal-fired furnaces. In Sandia's Coal Combustion Laboratory (CCL), optical techniques are used to obtain high-resolution images of individual burning coal char particles and to measure, *in situ*, their temperatures, sizes, and velocities. Detailed models of combustion transport processes are then used to determine kinetic parameters describing the combustion behavior as a function of coal type and combustion environment. Partially reacted char particles are also sampled and characterized with advanced materials diagnostics to understand the critical physical and chemical transformations that influence reaction rates and burnout times. The ultimate goal of the task is the establishment of a data base of the high temperature reactivities of chars from strategic U.S. coals, from which important trends may be identified and predictive capabilities developed.

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

Subtask 1.1 Kinetics of Heterogeneous Fuel Particle Populations

The objective of this subtask is to develop quantitative descriptions of single-particle combustion behavior and to identify their implications for global rates and for the performance of combustion systems. Experiments in the CCL provide a wealth of unique information on the combustion behavior of single particles as distinguished from macroscopic samples. Kinetic expressions based on population statistics are being developed that more accurately describe the char combustion process as it proceeds into the important region of high carbon conversion. One-dimensional combustion models are being applied to char particle populations, exhibiting realistic heterogeneity in size and reactivity, to identify the important mechanisms leading to unburned carbon in fly ash.

Subtask 1.2 Char Combustion Kinetics to High Carbon Conversion

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

Subtask 1.3 The Role of Particle Structure and the Char Formation Process in Combustion

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

Subtask 1.4 Unification of Sandia Char Combustion Data Base

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

SUMMARY OF TECHNICAL PROGRESS DURING THIS QUARTER

Work this quarter focused on subtasks 1.1 and 1.3, and culminated in the development of a combustion kinetic model for heterogeneous solid fuels. To provide data for the heterogeneity model, captive particle imaging (CPI) experiments were conducted on a series of coals of various rank to elucidate the relationships between reactivity, ash content, and swelling behavior. Experiments were carried out on a high rank coal, Pocahontas #3, PSOC-1508D, and on two low-rank coals, Beulah lignite, PSOC-1507D, and Dietz subbituminous, PSOC-1488D. These experiments also represent the first application of the captive particle technique to raw coals, rather than prepared chars.

In addition, high resolution transmission microscopy fringe images were obtained of a series of partially combusted chars from the high rank Pocahontas #3 coal to examine the effect of rank on the dynamics of char carbon crystalline rearrangements. Development of the heated-wall reactor system continued this quarter, and the reactor was used to generate partially-reacted samples of four coals from the PETC suite. The captive particle imaging experiments and the heterogeneity model development are described in detail below.

Captive Particle Imaging Experiments

A key goal of this project is to understand the origin and implications of the broad distributions of single-particle temperature observed during char combustion under boiler-relevant conditions. Work to date has shown that the temperature distributions are caused primarily by reactivity differences at low conversion [Hurt, 1993], and by the presence of highly-reacted, high ash-content particles at higher conversions [Mitchell, 1990]. A number of other researchers have investigated fuel heterogeneity through single particle combustion experiments [Sahu et al., 1988, Wall et al., 1992], studies on lithotypes or maceral concentrates [Thomas et al., 1993, Crelling et al., 1992], or reflected light analysis of combustion residues [Bailey et al., 1990; Nandi, et al., 1977, Shibaoka, 1985, Morley and Jones, 1986, Oka et al., 1987]. Based on the existing body of work, the reactivity distributions that result from the inherent heterogeneity in coal are expected to be very significant in determining total burnout times due to the longevity of the low-reactivity tail of the distribution.

In order to understand and describe reactivity distributions, more information is needed about their origin, in particular about the origin of the low-reactivity tail of the distribution. If the low-temperature, low-reactivity particles are also the particles with high density, their burnout times, which are related to the product of reactivity and density, will be extremely long. If on the other hand, the low-temperature, low-reactivity particles are those of unusually high ash content, their carbon contents will be low and their burnout times will be much shorter. Assessing the technological significance of the reactivity distributions hinges on understanding the relationship between reactivity on the one hand, and particle density and ash content on the other. Captive particle imaging experiments in the dual imaging mode were therefore carried out on raw coals to allow simultaneous measurement of particle temperatures (which are indicators of particle reactivity), swelling factors (which are indicators of char particle density), and final ash particle sizes (which are indicators of ash content). The samples selected and the experimental procedures are described in detail below.

Samples and Experimental Procedures

Captive particle imaging experiments were performed on the following four coals spanning a wide range of rank: Pocahontas #3, PSOC-1508D, low-volatile bituminous; Illinois #6, PSOC-1493D, high-volatile bituminous; Dietz, PSOC-1488D, subbituminous; and Beulah lignite, PSOC-1507D. Raw coal particles (rather than preprepared chars) were used to provide information on swelling behavior. The raw coal particle diameters ranged from 125 - 250 μm .

The basic captive particle experiment has been thoroughly described in previous papers and reports [Hurt and Davis, 1994, Hurt et al., 1993, Hurt et al., 1994]. The dual camera configuration was used in the current work to allow quantitative measurements of particle radiance temperatures. For each particle, the image sequences were processed to determine: (1) a swelling factor, (2) a maximum particle radiance temperature (as a measure of reactivity), and (3) the ratio of the ash particle size (at the end of the sequence) to the initial coal particle size, d_a/d_c . This ratio is a convenient and useful indicator of initial ash content, although it cannot be quantitatively related to ash mass fraction due to variations in carbon density, ash densities and vaporization losses. In order to be a meaningful indicator of reactivity, the particle temperature must rise measurably above the local gas temperature and yet not exceed the value that results in detector saturation. To achieve these conditions, the gas temperature and oxygen concentration were adjusted for each coal. The low-rank coals (Dietz and Beulah) were combusted in 3 mole-% oxygen at a gas temperature of 1173 K, the Illinois coal in 6 mole-% at 1250 K, and the Pocahontas in 19 mole-% oxygen at 1250 K.

The particle sizes reported are averages of (1) the overall maximum particle dimension and (2) the maximum dimension perpendicular to the principal axis (along which the overall maximum dimension lies). These two dimensions are equivalent to those of a rectangle drawn around (tangential) to the particle and aligned along the principal axis. The swelling factor is defined as the ratio of the maximum char particle diameter to the initial coal particle diameter. To determine the maximum particle radiance temperature, the video field with the brightest particle incandescence was identified, the image digitized, and the average gray scale determined. Gray scales were then converted to particle radiance temperatures by calibrating the microscope optics and camera with a high-temperature blackbody source equipped with a microscope attachment [Hurt et al, 1994].

Experimental results

Single-particle swelling factors, $d_{\max}/d_c$, for the four coals are summarized in Fig. 1.1. The low rank coals exhibit single-particle swelling factors from 0.75 to 1.35, with the distribution roughly centered about 1 (no swelling). Measurement errors are estimated to be less than 5%, and thus both real swelling and contraction do occur for these materials on a single particle basis. These results are consistent with bulk swelling factors of 0.85 - 1.16 estimated previously for low rank coals by measurements of tapped bed density [Mitchell et al., 1992].

The Illinois #6 coal exhibits high swelling factors, from 1.05 - 2.1, while the high-rank, low-volatile Pocahontas coal exhibits lower swelling factors that lie consistently in a narrow range from 1.0 to 1.25. Bulk swelling factors from Mitchell et al. [1992] were measured to be 1.06 for the Illinois coal and 1.27 for the Pocahontas. The differences may be related to differences in heating rates, which have been estimated as $5 \cdot 10^4$ K/sec in the flow reactor experiments and $2 \cdot 10^3$ K/sec in the CPI experiments. Swelling factors have been shown to be strongly dependent upon heating rate, and often pass through a maximum as heating rate increases [Melia and Bowman, 1983].

Figure 1.1 Summary of single-particle swelling factors determined by captive particle imaging.

The data from image processing were examined in search of possible correlations between the temperature, ash, and swelling measurements. Figures 1.2 - 1.4 show examples for the Illinois #6 coal of single-particle temperature measurements plotted vs. d_a/d_c , initial coal particle diameter, and swelling factor, respectively. No strong correlations were found for any of the coals between single-particle temperatures on the one hand, and ash contents, swelling factors, or particle sizes on the other.

In the early stages of combustion it is clear that single particle reactivity varies greatly and is not closely related to ash content or swelling behavior. In particular, the lowest temperature (reactivity) particles observed were not unusual in either their apparent ash contents[†] or in their swelling behavior. It is a useful and justifiable approximation to assume that the distributions of reactivity, swelling factor, and ash content are mutually *independent*. This is a key result that will guide the modeling work described in the next section.

[†] Note that this conclusion relates to the early stages of the combustion process, before significant numbers of highly-reacted, ash-rich particles appear. Highly oxidized particles with very high ash contents are expected to have low global reactivities due to the "dilution" effect [Hurt and Davis, 1994], and indeed are responsible for many of the low-temperature particles observed at high conversions [Mitchell, 1990].

Figure 1.2 Single-particle measurements for Illinois #6 coal char: maximum temperature as a function of the ratio of ash particle diameter to coal particle diameter.

Figure 1.3 Single-particle measurements for Illinois #6 coal char: maximum temperature as a function of coal particle diameter.

Figure 1.4 Single-particle measurements for Illinois #6 coal char: maximum temperature as a function of swelling factor.

Development of a Kinetic Model for Heterogeneous Solid Fuels

The ultimate goal of Task 1 work in FY94 is the development of an advanced model of carbon burnout, incorporating (1) a submodel of heterogeneity and (2) a submodel of conversion or time-dependent changes in char structure and reactivity. In this section, a submodel of the kinetics of heterogeneous particle populations is developed and tested. The validated submodel is then used in a one-dimensional simulation to illustrate the effect of heterogeneity on carbon burnout.

Measured temperature distributions

The model will be tested by its ability to predict the set of measured temperature distributions for the suite of ten PETC coals undergoing combustion in both 6 and 12 mole-% oxygen. Of primary interest is the overall breadth of the distribution, represented by the variance, σ_A^2 . Before the temperature variances can be compared to the predictions of the heterogeneity model, the raw data must be treated to remove several interfering effects.

First, at high conversion, the temperature variances are strongly influenced by the presence of numerous low-temperature particles identified by Mitchell [1992] as highly-reacted, high-ash-content particles. This is a conversion-dependent effect that makes these distributions unsuitable for characterizing heterogeneity in the parent fuel. For this

analysis, therefore, we consider only that subset of the optical data for which bulk char carbon conversions are less than 45%. Secondly, at the earliest residence time (72 msec) a very small number of particles are often observed at or below the local gas temperature which are absent at the next measurement point (95 msec). These particles are believed to be in the latter stages of transient heating at the earliest residence time, but to have reached their pseudo-equilibrium temperature by 95 msec. These few particles have a negligible effect on the overall temperature variance when it is broad, but can contribute significantly when the remainder of the distribution is narrow. Therefore, the few particles at the earliest residence time that are at or below the local gas temperature were removed from the raw data for these analyses. The remaining data, which serve as the basis set for developing and validating the heterogeneity model, is shown in Fig. 1.5. In this data set the temperature variances range from 324 K^2 ($\sigma = 18$ K) to 8650 K^2 ($\sigma = 93$ K).

Figure 1.5 Measured and predicted temperature variances for various coal chars burning in various combustion environments. Symbols are measured variances; dashed lines are model predictions.

Model formulation

Carbon conversion, or extent of burnout, is affected by the distributions of both reactivity, $A^\dagger$, and particle density, ρ . To describe heterogeneity, we therefore seek a function, $F(A, \rho)$ that represents the joint distribution of reactivity and density in the char particle population. The most important contributors to the variations in particle density are believed to be variations in swelling factor and ash content. The experimental results presented above indicate that particle-to-particle variations in reactivity are largely independent from variations in swelling factor or ash content, suggesting the following model formulation:

$$F(A, \rho) = F_A(A) + F_\rho(\rho) \quad (1.1)$$

We therefore seek two independent functions, F_A and F_ρ describing the heterogeneity in reactivity and density, respectively. The following section treats the reactivity distribution function, while the density distribution function is reserved for the next report. The reactivity distribution function, F_A , should be a property of a given char and independent of combustion conditions. It remains to be seen if a single, coal-independent F_A function can be defined that will describe the data set for the entire suite of ten PETC coals, or if F_A must be determined for each coal of interest.

A functional form must first be chosen to describe the reactivity distributions, $F_A(A)$. Gaussian distributions were deemed inappropriate as their tails extend to negative values for chars with low mean reactivities. Log-normal distributions do not suffer the problem of negative reactivities, but were observed to produce poor fits of the measured temperature distributions. Gamma distributions were ultimately chosen for the functional form of the reactivity distribution distributions, defined by:

$$F_A(A) = \frac{e^{-\beta A}}{\Gamma(A)} A^{\alpha-1} \beta^\alpha \quad (1.2)$$

where α and β are the distribution parameters and $\Gamma(A)$ is the gamma function. The gamma reactivity distribution, $F_A(A)$, is defined only for $A > 0$, and has the convenient

[†] Variations in particle reactivity arise due to variations in the intrinsic reactivity, k_i , surface areas, S , and effective diffusion coefficients, D_{eff} . The variations in intrinsic reactivity can affect the temperature dependent term (such as the activation energy, E_i , in Arrhenius kinetics) or the temperature independent term (such as the preexponential factor, A_i , in Arrhenius kinetics). Of the four parameters S , D_{eff} , A_i , E_i , variations in three of them (S , D_{eff} , A_i) appear as variations in the global preexponential factor, A . Only variations in E_i will affect the global activation energy, E , and E_i has been shown to fall within a narrow range of values for a wide variety of impure carbons. Therefore, the model is based on an explicit description of variations in A , as a convenient approximate representation of the total heterogeneity.

property that the mean and variance are simple functions of α and β :

$$A_{mean} = \alpha / \beta \quad (1.3a)$$

$$\sigma_A^2 = \alpha / \beta^2 \quad (1.3b)$$

The complete reactivity distribution function was determined as follows. Relationships between preexponential factors and particle temperatures were first determined by solving, for each combustion condition of interest, the coupled mass and energy transport equations describing burning char particles [Mitchell, 1988]. Note that because the heterogeneity model is designed as an extension of the global kinetic model of Hurt and Mitchell [1992], these calculations adopt mean parameters from this model, namely a global reaction order, $n = 0.5$, a global activation energy of 20 kcal/mol, and a CO/CO₂ product ratio equal to $3.10^8 \exp(60,000/RT_p)$, where RT_p has the units cal/mole, and T_p is the particle temperature. Then, for each coal, a mean value of the preexponential factor, A_{mean} , was determined to best match the mean particle temperatures measured optically.

The distribution is then determined by choosing a value for the heterogeneity parameter, σ_A , computing α and β by Eq. 1.3, computing the distribution function by Eq. 1.2, computing the temperature distribution from the coupled mass and energy balances, and then comparing the predicted temperature variances with the measured variances in Fig. 1.5. A Newton-Raphson algorithm was then used to find the single value of the heterogeneity parameter, σ_A , that minimizes the sum of squared residuals between the predicted and measured variances for the entire data set in Fig. 1.5.

The model predictions are shown as dashed lines in Fig. 1.5. A single, coal-independent value of the heterogeneity parameter, σ_A , is seen to provide a good description of the entire set of single-particle temperature distributions. This is also illustrated in Fig. 1.6, which plots the measured values of temperature variance versus those predicted by the model. Fig. 1.7 gives an example comparison of measured and predicted particle temperature distributions, along with the gamma distribution of preexponential factors on which the prediction is based.

The success of this simple model indicates that the large coal-to-coal differences observed in the temperature variance do *not* reflect differing degrees of fuel heterogeneity. Rather, the extent of fuel heterogeneity is nearly constant across this sample set, but the varying combustion conditions give rise to the wide range of temperature variances (324 to 8650 K²). The large temperature variances arise at those combustion conditions, at which the governing gas-particle transport relations exhibit a high sensitivity of particle temperature to reactivity. Such conditions include high oxygen concentrations and mean reaction rates far from the boundary layer diffusion limit.

Figure 1.6 Predicted vs. measured temperature variances.

This is illustrated in Fig. 1.8, where the relationship between reactivity, A , and particle temperature, T_p , is presented for a single, selected gas environment[†]. In Fig. 1.8, char particle temperature is 1515 K at zero reactivity and increases with increasing reactivity up to a nearly asymptotic temperature at reactivities greater than $A = 40$ as the diffusion limit is approached. The sensitivity of temperature to reactivity is the slope of this plot, $\delta T_p / \delta A$, and decreases from 30 to 4 as reactivity increases from 5 to 30. Thus, under these conditions, reactive chars that burn close to the boundary layer diffusion limit will have narrower temperature distributions than less reactive chars that burn further from the diffusion limit.

[†] Note that this same relationship, plotted as the logarithm of the global rate coefficient vs. $1/T_p$, has been used in the analysis of combustion kinetics [Hurt and Mitchell, 1992b] and extinction phenomena [Hurt, 1993], where it has been referred to as a "characteristic curve" representing the gas-particle transport relations.)

Figure 1.7 Example of measured and predicted particle temperature distributions for Pocahontas #3 coal char. Combustion conditions are 12 mole-% oxygen and a gas temperature of 1645 K. Shown in the inset is the gamma distribution of preexponential factors on which the prediction is based.

Figure 1.8 Relationship between reactivity and particle temperature determined by the gas-particle transport equations. Combustion conditions: 100 μm diameter particles, 12% oxygen, gas temperature 1645 K.

The success of this simple approach indicates that the major effects of fuel heterogeneity on burnout can be captured with a model that does not require detailed coal-specific characterization. The coal-general heterogeneity model developed here can be conveniently incorporated into one-dimensional carbon burnout models or into carbon burnout post processors on multi-dimensional simulators.

Implications for carbon burnout

A one-dimensional simulation was carried out to demonstrate the implications of heterogeneity for carbon burnout behavior. Starting with the gamma distribution of preexponential factors determined above for Pocahontas #3 ($A_{\text{mean}} = 7.5$, $\sigma_A = 3.95$), the combustion of a collection of 100 μm diameter Pocahontas char particles was simulated in an isothermal gas environment of 1600 K containing 12 mol-% oxygen. The combined kinetic and transport equations were solved to obtain extents of mass loss as a function of time for each reactivity fraction present in the initial char, and the results were weighted and

combined to compute carbon conversions for the overall sample. For comparison, a burnout profile was computed for a uniform sample in which each particle has the mean preexponential factor of $7.5 \text{ g-carbon cm}^{-2} \text{ s}^{-1} \text{ atm}^{-0.5}$.

The results are shown in Fig. 1.9. The uniform and heterogeneous samples burn at comparable rates up to about 70% carbon conversion, after which they diverge sharply. To reach 95% carbon conversion, the heterogeneous sample requires twice the residence time of the uniform sample. To reach 98% carbon conversion, the heterogeneous sample requires a factor of 3.4 greater residence time than the uniform sample. Clearly, for the very high carbon conversions required for economic operation of commercial boilers, heterogeneity can play an important role.

Figure 1.9 Comparison of carbon burnout behavior predicted by the uniform and distributed reactivity models. Sample: Pocahontas #3 coal char, initial particle diameter $100 \mu\text{m}$. Combustion conditions: 12 mole-% oxygen, isothermal gas at 1500 K.

Conclusions

1. The Sandia captive particle imaging technique has been used to elucidate the relationships between reactivity, ash content, and swelling behavior on a single-particle basis.
2. A statistical model of char heterogeneity has been developed based on gamma distributions of single-particle reactivity. The model incorporates a single empirical heterogeneity parameter, σ_A , common to all coals and conditions, and is capable of explaining the entire set of measured temperature distributions at low conversion for the PETC suite of ten coals.
3. The success of the simple heterogeneity model indicates that the large coal-to-coal differences observed in the temperature variance do *not* reflect differing degrees of fuel heterogeneity. Rather, the extent of fuel heterogeneity is nearly constant across this sample set, but the varying combustion conditions give rise to the wide range of temperature variances (324 to 8650 K²). This implies that the major effects of fuel heterogeneity on burnout can be usefully modeled without detailed coal-specific characterization.
4. A one-dimensional simulation has demonstrated the effect of fuel heterogeneity on carbon burnout. For a specific example of Pocahontas #3 char reacting in 12 mole-% oxygen at a gas temperature of 1600 K, heterogeneity increases the time required to reach 98% by a factor of 3.4.
5. The coal-general heterogeneity model developed and presented in this report is designed as an extension of the global kinetic model of Hurt and Mitchell [1992], and is suitable for incorporation into one-dimensional carbon burnout models or into carbon burnout post processors on multi-dimensional simulators.

PLANS FOR NEXT QUARTER

During the next quarter, particle density distributions will be incorporated into the heterogeneity submodel, completing the planned work under Subtask 1.1. Captive particle imaging results will also be analyzed to compare extinction behavior at high conversion for coals of various rank, thus completing Subtask 2.3. Finally, the first formulation of a char deactivation model will be attempted next quarter and more long residence time, high-conversion data will be taken in the heated-wall reactor system.

ACKNOWLEDGMENTS

Financial support for this work is provided by the U.S. DOE Pittsburgh Energy Technology Center's Direct Utilization Advanced Research and Technology Development Program. The technical contributions of James Ross of TAD technical services are gratefully acknowledged.

NOMENCLATURE FOR TASK 2

A, A_{mean}	reactivity or global preexponential factor, mean reactivity, g-carbon cm^{-2} -external surface $\text{s}^{-1} \text{atm}^{-n}$
A_i	intrinsic preexponential factor, g-carbon cm^{-2} -total surface $\text{s}^{-1} \text{atm}^{-n}$
d_a, d_c, d_{max}	particle diameters: ash, unreacted coal, and maximum, respectively, μm
D_{eff}	effective diffusion coefficient in porous char particles, cm^2/s
E, E_i	global activation energy, intrinsic activation energy, kcal mole^{-1}
F_A	reactivity distribution function, $F_A dA$ is the number of particles with reactivities between A and $A+dA$
F_ρ	density distribution function
k	global chemical reaction rate coefficient, g-carbon cm^{-2} -external surface $\text{s}^{-1} \text{atm}^{-n}$
k_i	intrinsic chemical reaction rate coefficient, g-carbon cm^{-2} -total surface $\text{s}^{-1} \text{atm}^{-n}$
n	global reaction order
q	overall particle burning rate per unit external surface area, $\text{g C cm}^{-2} \text{s}^{-1}$
R	gas constant, $\text{kcal mole}^{-1} \text{K}^{-1}$
S	total surface area, m^2/g
T_g	gas temperature, K
T_p	particle temperature, K

Greek symbols

ρ	particle density, g/cm^3
σ_A, σ_{Tp}	standard deviation of reactivity, particle temperature

PUBLICATIONS, PAPERS, AND PRESENTATIONS

An article derived from research sponsored jointly by PETC and EPRI was accepted this quarter for publication in *Fuel*. A second paper in this series was submitted in June. Both references are given below, and copies of the manuscripts are included with this report.

Hurt, R. H. and Gibbins, J. R., Residual Carbon from Pulverized Coal Fired Boilers 1: Size Distribution and Combustion Reactivity, submitted to *Fuel*, 1994.

Hurt, R. H., Davis, K. A., Yang, N. Y. C., and Headley, T. R. "Residual Carbon from Pulverized Coal Fired Boilers 2: Morphology and Physicochemical Properties, in preparation for submission to *Fuel*, 1994.

In April, a paper was written and submitted for presentation at the Annual PETC Contractor's Conference to be held in Pittsburgh in July, 1994. Also in April, an invited seminar was given at Stanford University on the topic "Carbon Densification Mechanisms in Combustion," as part of the High Temperature Gas Dynamics Laboratory seminar series.

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PROJECT TITLE: COAL COMBUSTION SCIENCE

TASK 2: DEPOSIT GROWTH AND PROPERTY DEVELOPMENT IN COAL-FIRED FURNACES

ORGANIZATION: Sandia National Laboratories, Livermore

CONTRACT: FWP 0709

REPORTING PERIOD: April 1 - June 30, 1994

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

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

OBJECTIVES FOR TASK 2

Task 2 is a four-year project focused on the growth and properties of deposits generated in coal-fired furnaces. The project runs from Oct. 1993 to Sept. 1997. The objectives of this research project are: (1) to provide a self-consistent database of simultaneously measured, time-resolved ash deposit properties in well-controlled and well-defined environments, and (2) to provide analytical expressions that relate deposit composition and structure to deposit properties of immediate relevance to PETC's Combustion 2000 program. This project is distinguished from other projects in the same research area by: (1) the development and deployment of *in situ* diagnostics to monitor deposit properties, (2) the time resolution of such properties during deposit growth, (3) simultaneous measurement of structural and composition properties, (4) development of algorithms from a self-consistent, simultaneously measured database that includes the interdependence of properties, and (5) application of the results to technologically relevant environments such as those being planned under the Combustion 2000 program. The deposit properties of principal interest in this project include the heat transfer coefficient, porosity, emissivity, tenacity, strength, density, and viscosity.

The first year is primarily associated with diagnostic development. This includes major activities associated with two *in situ*, real-time diagnostics for measuring inorganic materials on surfaces and in the gas-phase. Also, several diagnostics are being incorporated into Sandia's Multifuel Combustor (MFC) that will eventually be used to characterize ash deposit properties.

The research project is divided into six subtasks. The titles and objectives of these subtasks are summarized below, followed by a discussion of progress this quarter.

Subtask 2.1 Diagnostics for Coal Combustion Environments

The objective of this subtask is to develop and demonstrate diagnostics capable of *in situ* measurement of: (1) condensed-phase species on surfaces in combustion environments, and (2) inorganic vapors in turbulent, particle-laden, combustion gases.

Subtask 2.2 Experimental Determination of Transport, Thermal, and Structural Properties of Ash Deposits

The objective of this subtask is to provide self-consistent, simultaneous measurement of ash deposit properties under combustion conditions that simulate commercial-scale environments such as those expected to occur in Combustion 2000 technologies. Properties to be measured simultaneously and in real time include thermal conductivity, emissivity, porosity, mass and volume rate of growth, surface composition, and tenacity. Additional properties to be measured, but not in real time or *in situ*, include bulk elemental composition, bulk species composition, shear strength, true density, and detailed morphology.

Subtask 2.3 Analysis of Deposit Properties

The objective of this subtask is to provide an analytical capability for describing the development of deposit properties in combustion systems. Deposit properties to be predicted by this analytical method are similar to those discussed in Subtask 2.2 and include: (1) thermal conductivity, (2) emissivity, (3) porosity, (4) mass and volume rate of growth, (5) surface composition, (6) tenacity, (7) bulk elemental composition, and (8) major species composition.

Subtask 2.4 Chemical Reactions in Deposits

The objective of this subtask is to determine rates and mechanisms that describe chemical reactions in coal ash deposits that alter their properties or their morphology. This subtask is more limited in scope than the previous subtasks. We do not intend to conduct a comprehensive study of inorganic chemistry as it relates to ash deposits. We do intend to review available literature and perform calculations that allow us to capture the first-order terms that describe changes in deposit chemistry with time. This work will result in usable results, but is limited to global kinetics and simplified chemical mechanisms that outline the nature of the reactions and their dependence on operating parameters. The details of the kinetics will not be studied.

Subtask 2.5 Application to Combustion 2000 Program

The objective of this subtask is to exchange technology developed under other subtasks with ongoing Combustion 2000 efforts by other PETC contractors.

Subtask 2.6 Documentation

The objective of this subtask is to provide timely and accurate documentation of project progress, major milestones, and publishable results.

SUMMARY OF TECHNICAL PROGRESS DURING THIS QUARTER

Subtask 2.1 Diagnostics for Coal Combustion Environments

Tunable Diode Laser Diagnostic

Summary

During this quarter, characterization of the tunable diode laser (TDL) was conducted over a broad range of currents and diode temperatures (Figs 2.1 through 2.9). The TDL is tunable by either varying current or temperature of the diode. The particular diode being used in this experiment operates at frequencies near 400 cm^{-1} ($25\text{ }\mu\text{m}$). This represents the far infrared limit for currently available diodes, and the diode tends to lase at several frequencies. The objective of our current investigation is to determine the frequencies at which the diode lases under a given set of conditions of current and temperature. As either current or temperature increases, the frequencies of a given line from the laser increases.

Background

The generation of inorganic vapors has long been cited as a feature of particle reaction during coal combustion [Beér, et al., 1990; Benson, et al., 1993; Helble, et al., 1986; Helble and Sarofim, 1989; Neville, et al., 1980; Neville and Sarofim, 1985; Quann, et al., 1982; Quann, et al., 1990; Quann and Sarofim, 1982; Wibberley and Wall, 1986; Zygarlicke, et al., 1992]. Atomically dispersed or other forms of the alkali and alkaline earth material in coal that are not thermally or chemically stable contribute to these vapors. Such material leaves coal particles to form vapors by at least two mechanisms: classical vaporization and in conjunction with coal devolatilization products [Baxter, et al., 1994 (to appear); Neville, et al., 1980]. The majority of the studies of this material are based on elemental analyses of particulates sampled from a coal combustion flow. Typically, such samples exhibit a concentration of submicron particulates that is enriched in alkali and alkaline earth material relative to the more refractory materials. The appearance of material in the small size fractions is typically taken as an indicator of vaporization and condensation of the material.

This research contributes significant knowledge to the behavior of inorganic material during combustion. However, transformations of the vapors that occur during combustion and during sampling complicate the analyses significantly. The traditional interpretation of data supposes that inorganic vapors nucleate and condense to form small particulates or an aerosol. Analyses of this aerosol provides an indication of the amount of vapor that was originally present. Condensation of the vapor on probe surfaces and other particulates, both sub- and supermicron, and the presence of submicron particulates that did not go through a vaporization step are among the complications that are difficult to satisfactorily resolve when dealing with solid samples. In addition, reliable means of determining the specific chemical species from which the submicron material is generated on the basis of the solid analyses have not been developed. Additional issues involve translating aerodynamic diameters to true diameters to obtain accurate estimates of total mass, sampling selectivity and collection efficiency as a function of diameter, and obtaining representative, reproducible samples from potentially striated flows in ducts and reactors.

Many of the complications involved in these traditional approaches to sample collection could be avoided if direct means of measuring the vapors could be developed. Several attempts have been made to more directly measure the concentration of the inorganic vapors in coal combustion flows. Laser-induced photodissociation and fluorescence is one such technique [Helble, et al., 1992; Oldenberg and Baughcum, 1986]. The technique is based on the detection of a material, say sodium, independent of its chemical form. However, the experiments were devised to allow NaCl to be the dominant contributor to the measured signal. While the technique has promise, in some cases it was difficult to demonstrate consistently reasonable trends with changing coal feed rate or other operating conditions.

Approach

In this subtask, we measure the presence of inorganic vapors directly in a species-specific way in realistic coal combustion environments. The technique for performing such measurements is absorption spectroscopy using tunable diode lasers (TDL). This technique uses solid-state lasers that can be tuned by biasing the current through the diode. Typically, a given diode can be tuned over a range of 30-50 cm^{-1} , with a resolution of better (lower) than 0.01 cm^{-1} . Different diodes can be selected to allow access to different regions of the infrared spectrum. The regions of interest in this study are in the far infrared, where hydroxides, chlorides, and oxides of the alkali and alkaline earth materials have infrared-active, rotational-vibrational transitions. The specific locations of the transitions are being determined using high-resolution FTIR spectroscopy in a hot sample cell in collaboration with Prof. Peter Bernath (Univ. of Waterloo) and Dr. Ram Ram (Univ. of Arizona).

Inorganic vapor concentrations will be directly measured *in situ* in the test section of the MFC under this subtask. Some of this work will be performed collaboratively with Dr. Peter Bernath, University of Waterloo, Canada. This investigation is further divided into six subprojects. A suitable diode laser cold head is available, together with a diode laser that should be able to detect sodium and potassium hydroxide. However, the diode laser still needs to be characterized and suitable means of detecting the beam need to be evaluated. The same cold head with a completely functioning laser appropriate for CO and CO₂ detection are also available.

The spectral absorptivities of the hydroxides and chlorides of interest will be investigated using high-resolution FTIR transmission spectroscopy in conjunction with a high temperature gas cell in idealized, controlled environments. The FTIR work will be completed in Canada, where an appropriate gas cell and spectrometer are available. These spectra will be used to identify a bandhead or other appropriate spectral feature that can be used to measure inorganic vapor concentrations. The TDL will be tuned across the spectral feature, and absorption spectroscopy will be used to measure the concentration of the inorganic vapor.

The TDL will first be used to measure CO or CO₂ concentrations in the MFC test section. The present system has a functioning laser and detector for measuring these species. The measurements will be made in the mid-infrared region where both interference from other species and logistics of operating the laser are less of an issue. These tests will allow us to develop the technique and to prove its applicability on less demanding material, while also characterizing the laser to be used for the inorganic hydroxides.

The first experiments on inorganic vapors will focus on alkali hydroxides, these being among the most thermodynamically stable alkali-containing vapors in the absence of halides (chlorine). The band centers of the metal-oxygen stretch frequencies have been reported at 431 cm^{-1} and 408 cm^{-1} for NaOH and KOH, respectively. These will be confirmed and more extensive information will be obtained in collaboration with Prof. Bernath. Diode lasers that operate in this region are commercially available, but they must be operated at or below 25 K. The closed-cycle helium refrigerator cold head available to us is suitable for this application. The chlorides are even more stable than the hydroxides. The presence of chlorine in the coal is believed to result in the formation of alkali chloride vapors [Srinivasachar, et al., 1990]. The reported fundamental vibrational modes of these compounds (362 and 279 cm^{-1} for sodium and potassium chloride, respectively) are below the low wavenumber limit of tunable diode lasers ($\approx 390\text{ cm}^{-1}$). While there is a possibility that they could be detected by looking for overtones, additional techniques may be required to detect them reliably. In this work we will attempt to find their overtones as a scoping study, but we plan to focus on the hydroxides rather than the chlorides.

Experimental Results and Discussion

Figure 2.1 illustrates typical TDL data. The output from the laser is shown at one diode current (270 mA) at five temperatures (5-25 K). The lines are labeled accordingly (i330T10 represents a current of 330 mA and a temperature of 10 K). Each scan is offset by 0.1 V along the ordinate. There is no offset along the abscissa. The number of major laser modes varies from two to seven, increasing with increasing temperature. The temperatures reported here are based on a manufacturer calibration of cold head temperature versus potential. The temperature we call 5 K is out of the range of calibrated values on the low temperature side. The remaining temperatures are in the range of the calibration. However, we believe the absolute magnitude of the temperature may be in error by as much as 5 K. Such an error is irrelevant to the experiment. The temperatures are only used as metrics to return the laser to some known state.

The two important issues to note in Figure 2.1 are (1) the shift in frequency with increasing temperature, and (2) the behavior of the laser at the low wavenumber end. The shift is related to the tunability of the laser. Data such as those shown in the figure are used to determine the conditions required to attain the desired lasing frequency. We will return to the low-wavenumber behavior later.

Data similar to those illustrated in Fig. 2.1 were collected every 30 mA from 270 to 480 mA. Currents greater than 500 mA can potentially damage the diode whereas currents less than 270 mA are insufficient to excite the diode into a laser mode. Similarly, the data were collected every 5 K from 5 K to 25 K. Lower temperatures are not achievable by our cryogenic compressor and the laser structure deteriorates as the temperature increases significantly above 25 K.

Figures 2.2 through 2.9 illustrate the remaining data in the same format used in Fig. 2.1. The same general pattern is seen in these data as is illustrated in Fig. 2.1. These spectra were collected using a FTIR spectrometer (Digilab FTS-60) at 0.5 cm^{-1} resolution. The laser line-widths are about 0.05 cm^{-1} . Therefore, the line-shapes in the figures are dominated by the instrument line-shape and not the beam line-shape in these plots. The FTIR spectrometer line-shape for unapodized spectra (such as these) is $\text{sinc}(x)$ ($\sin(x)/x$).

Figure 2.1 Tunable diode laser behavior as a function of temperature at a current of 270 mA for frequencies between 380 and 430 μm .

The addition of high wavenumber components and loss of low wavenumber components in the laser beam with increasing diode temperature is also a common and expected feature. A similar trend is seen as current increases at constant temperature (Fig. 2.9), although the addition of new modes is more sensitive to temperature than current over the ranges illustrated here. These trends are consistent with our expectations.

Sodium and potassium hydroxide species are reported to have spectra within the range of this laser. We are currently obtaining high temperature spectra for these vapor species for use as a reference (in collaboration with Prof. Peter Bernath of the Univ. of Waterloo). The chlorides are also potentially important to ash deposition. They exhibit spectral bands at or near the low end of the range of our TDL. Potassium chloride is beyond our range. The highest bandhead from sodium chloride is at about 487.7 cm^{-1} . This corresponds with the extreme edge of the range of

Figure 2.2 Tunable diode laser behavior as a function of temperature at a current of 300 mA for frequencies between 380 and 430 μm .

Figure 2.3 Tunable diode laser behavior as a function of temperature at a current of 330 mA for frequencies between 380 and 430 μm .

Figure 2.4 Tunable diode laser behavior as a function of temperature at a current of 360 mA for frequencies between 380 and 430 μm .

Figure 2.5 Tunable diode laser behavior as a function of temperature at a current of 390 mA for frequencies between 380 and 430 μm .

Figure 2.6 Tunable diode laser behavior as a function of temperature at a current of 420 mA for frequencies between 380 and 430 μm .

Figure 2.7 Tunable diode laser behavior as a function of temperature at a current of 450 mA for frequencies between 380 and 430 μm .

Figure 2.8 Tunable diode laser behavior as a function of temperature at a current of 480 mA for frequencies between 380 and 430 μm .

Figure 2.9 Tunable diode laser behavior as a function of current at a temperature of 10 K for frequencies between 380 and 430 μm .

the TDL. When we initiated this experiment, it was not clear that we would be able to observe any chlorinated species directly. It now appears possible that we can observe sodium chloride species directly. Potassium chloride will have to be measured using harmonics of the lower-lying spectral bands.

Other species of interest include sulfates and oxides of alkali metals. The sulfates should be easily observable, albeit with perhaps a different diode than the one currently being used. The oxides may be more difficult. Our project plan calls for completing the hydroxides first, followed by pursuit of other species. Therefore, our focus in the next report will be on hydroxides and possibly chlorides.

This diagnostic has the potential of quantitatively measuring the concentrations of alkali vapors *in situ*, in real time, nondestructively, and nonintrusively. These data will play an important role in the validation and development of ash deposit formation and fly ash formation.

A closer examination of the low wavenumber limit of the TDL indicates that, within the resolution and wavenumber accuracy of the instrument, we should be able to detect the highest frequency bandhead of the NaCl spectrum. Figure 2.10 illustrates the experimental spectral signature of NaCl. As is seen, the high wavenumber bandhead is located at about 387.8 cm^{-1} , which when compared to Fig. 2.9 coincides almost exactly with the low wavenumber limit of the TDL. It appears that we will either narrowly succeed or narrowly miss the opportunity to measure NaCl concentrations directly. In any event, the TDL is well suited for measurement of alkali hydroxide species, which are believed to be more important for combustion of nonchlorinated coals (including most US coals).

Subtask 2.2 Experimental Determination of Transport, Thermal, and Structural Properties of Ash Deposits

During the past quarter several problems with the deposit thickness measuring technique were resolved. In addition to the regular Sandia staff, Prof. Brian Jenkins (UC Davis), who is spending his sabbatical year at Sandia working on ash-related issues, has contributed to this portion of the work. The problems addressed in the last quarter include interface issues with the data acquisition computer, motor vibration in the stepper motors, mechanically generated noise in the data, and instabilities in the cantilevered arm of the device. There remain residual issues to be resolved, and a more complete description of the system will be presented in the future. In this section we present some results to provide an indication of the current status of the project.

Figure 2.11 illustrates data obtained from a machined, flat surface onto which two strips of tape were applied. The ordinate of the figure represents the height of the surface features relative to an arbitrary baseline that, in this case, is taken near the average surface position. The abscissa represents distance traveled by the diagnostic along a linear path parallel to the surface. The four major spikes in the figure represent the measurement of the positions of the two strips of tape. The first two were measured as the diagnostic traversed the plate in the forward direction. The latter two were measured during retraction of the diagnostic. The tape was determined by a micrometer to be about $150\text{ }\mu\text{m}$ thick.

Figure 2.10 Experimentally measured NaCl spectra (data from Prof. Peter Bernath) in the wavenumber range 383 to 388 cm^{-1} .

The figure illustrates reasonable behavior. The issues we continue to work on include the noise in the baseline and the systematic difference in the result depending on the direction in which the diagnostic is moving. Both are believed to be dominated by mechanical issues. The noise in the baseline has essentially the same periodicity as the travel of the lead screw that transports the diagnostic along its high-precision bearing. The lead screw completed twelve revolutions in this case, and there are about twelve major spikes apparent in the baseline. It would appear that the lead screw mechanical tolerance is too large, and we are seeking a higher precision component to replace the existing one. It is not clear whether surface roughness is also contributing to the noise in the baseline.

The systematic difference between the heights of the two strips of tape is also believed to be related to the motion of the diagnostic. The center two peaks in Fig. 2.10 should be mirror images (as should the outer two). Their height difference is related to a coupling between the cantilevered arm of the diagnostic and the torque in the lead screw. The profiles of the two strips of tape appear rounded because of the finite size of the laser beam ($\approx 1\text{mm}$) used to make the measurement. The diagnostic does not read the proper height until the beam is completely on the tape.

Figure 2.11 Results of trials with the deposit thickness diagnostic using a flat plate and two 150 μm thick strips of tape as references.

The diagnostic is currently in the form that can be applied to measuring ash deposit thickness *in situ*, in real time, nondestructively, and nonintrusively. While we continue to refine the details of the diagnostic, we plan to incorporate it in the standard experimental procedures used in the lab.

Subtask 2.3 Analysis of Deposit Properties

Considerable effort has gone into quantifying the effects of particle size, deposit porosity, and deposit composition on ash deposit emissivity and reflectivity during the last quarter. A theory that provides a useful framework is being pursued to determine the extent to which it can explain several observations. These observations and accompanying theory are being prepared for presentation at next month's contractor's review meeting. Figure 2.12 illustrates the issues. Two

Figure 2.12 Comparison of spectral emissivities for loosely aggregated fine particulate (<2 μ m) vs. modestly compressed samples of illite.

essentially identical samples of pulverized illite were examined for their radiative properties. One sample was a relatively porous (loose) collection of particles, whereas the other was modestly compressed to reduce porosity. The change in sample porosity has a pronounced influence on the spectral character of the deposits, as illustrated. Such influences are predicted within the framework of the theory we are developing. Further discussions of this issue will be included in forthcoming reports.

Subtask 2.4 Chemical Reactions in Deposits

We have begun investigating means of describing condensed phase equilibria for use in the reactions submodel of the algorithms for deposit properties. Several models have been identified,

most of which use either ideal solution theory or *ad hoc* methods of describing the condensed phase. Condensed phases of importance to this work are clearly non-ideal. Their non-ideal behavior represents some of their most important properties. We will continue to investigate these tools and report more fully on them in future reports.

Subtask 2.5 Application to Combustion 2000 Programs

During the past quarter, researchers visited with Combustion 2000 contractors at both Sandia and at the ORNL annual Fossil Energy Material Conference. We have identified a clear potential contribution of the FTIR spectroscopy work to the issue of ceramic corrosion. We are pursuing this at a modest priority. We are also pursuing involvement of the ASME Research Committee on Corrosion and Deposits in Combustion Gases in Combustion 2000 materials-related issues. In particular, the committee expressed some interest in an investigation of metallic corrosion studies of new materials at high temperatures in combustion environments.

Subtask 2.6 Documentation

During the last quarter, written papers and copies of slides to be used in the contractor's review meeting were submitted to PETC for review. Other documentation is discussed under publications and presentations below.

PLANS FOR NEXT QUARTER

On the ash deposition task, during the next quarter, TDL experiments will continue to be conducted in the MFC in pursuit of chlorides and hydroxides of sodium and potassium. To assist in this investigation, Professor Peter Bernath of the Department of Chemistry at the University of Waterloo will spend the month of July at Sandia. Dr. Bernath is an internationally recognized expert in chemical spectroscopy. Model compounds (pure chlorides or hydroxides) will be used for the initial tests. Latter tests will use commercially significant US coals with reasonably high alkali concentrations (e.g. Powder River Basin Coals). Also, the laser-based deposit thickness measurement diagnostic and the dynamic deposit weight diagnostic will be further developed. During August, Scott Sinquefield, a graduate student in the Department of Chemical Engineering, Oregon State University, will arrive to begin a one-year internship at Sandia. Scott is a member of Jim Frederick's group at OSU and will be working on a variety of projects related to ash behavior in coal and biomass combustion. The annual PETC contractor's review meeting is also scheduled during the next quarter and presentations summarizing our ash deposition-related work will be delivered at this conference.

ACKNOWLEDGMENTS

Sandia Contributors

Gian Sclipa and Al Salmi are instrumental in operating and maintaining the MFC and in assisting in the design and construction of diagnostic and probe equipment as well in conducting TDL experiments.

Industrial Contributors

Many of the chemical and physical analyses of solid samples of fly ash, deposits, and raw coal gathered during this investigation are performed by CONSOL Inc. with the assistance of Murray Abbott, Vince Conrad, and Diane Havekotte.

Academic Contributors

Mr. Galen Richards (Graduate Student, BYU) completed much of his PhD experimental work performing the FTIR measurements in the MFC and providing SEM images for analysis. Prof. John Harb (Brigham Young University) is his graduate advisor and collaborator in these efforts. Prof. Peter Bernath (Universities of Waterloo and Arizona) and Postdoctoral Associate Dr. Ram Ram (Univ. of Arizona) are collaborating in the collection and analysis of inorganic vapor species compositions at high temperature. Prof. Brian Jenkins (UC Davis) assists in many aspects of experimental and theoretical work. His contributions are primarily on other projects, but collateral contributions to this project, in particular the work on the deposit thickness measurement, are gratefully acknowledged.

PUBLICATIONS, PAPERS, AND PRESENTATIONS

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

Baxter, L.L., G. H. Richards, and J. N. Harb, "Dynamic Development of Deposit Properties During Coal Combustion," presented at the Eighth Annual ACERC Review Meeting and in preparation for publication.

Baxter, L.L., "Deposit Growth and Property Development in Coal-Fired Furnaces," presented at the DOE Office of Program Assessment Review, February, 1994, Pittsburgh, PA.

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