SANDIA REPORT

SAND2000-8253
Unlimited Release
Printed August 2000

Ash Deposit Formation and Deposit Properties

A Comprehensive Summary of Research Conducted at Sandia's Combustion Research Facility

Final Report

Larry L. Baxter

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.

RECEIVED
AUG 31 2000
OSTI

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Prices available from (703) 605-6000
Web site: <http://www.ntis.gov/ordering.htm>

Available to the public from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A11
Microfiche copy: A01

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SAND2000-8253
Unlimited Release
Printed August 2000

FINAL REPORT

Ash Deposit Formation and Deposit Properties: A Comprehensive Summary of Research Conducted at Sandia's Combustion Research Facility

Larry L. Baxter
Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94550 USA

Abstract

This report summarizes experimental and theoretical work performed at Sandia's Combustion Research Facility over the past eight years on the fate of inorganic material during coal combustion. This work has been done under four broad categories: coal characterization, fly ash formation, ash deposition, and deposit property development. The objective was to provide sufficient understanding of these four areas to be able to predict coal behavior in current and advanced conversion systems. This work has led to new characterization techniques for fuels that provide, for the first time, systematic and species specific information regarding the inorganic material. The transformations of inorganic material during combustion can be described in terms of the net effects of the transformations of these individual species. Deposit formation mechanisms provide a framework for predicting deposition rates for a broad range of particle sizes. Predictions based on these rates many times are quite accurate although there are important exceptions. A rigorous framework for evaluating deposit has been established. Substantial data have been obtained with which to exercise this framework, but this portion of the work is less mature than is any other. Accurate prediction of deposit properties as functions of fuel properties, boiler design, and boiler operating conditions represents the single most critical area where additional research is needed.

Table of Contents

<i>Ash Deposit Formation and Deposit Properties: A Comprehensive Summary of Research Conducted at Sandia's Combustion Research Facility</i>	<i>i</i>
<i>Table of Contents</i>	<i>ii</i>
<i>List of Figures</i>	<i>vi</i>
<i>List of Tables</i>	<i>xii</i>
Executive Summary	1
Fuel Characterization	2
Fly Ash Generation	2
Ash Deposition	2
Deposit Properties	3
Overall Conclusions	3
1. Introduction	4
2. Experimental Equipment	6
The Multifuel Combustor	6
In Situ, Real-time Diagnostics	7
Temperature-Controlled probes	9
Laser Triangulation Diagnostic	9
Optical Pyrometers	10
Fourier Transform Infrared Spectrometer	10
Particle Counter, Sizer, Velocimeter	11
Dynamic Balance	12
Integrated Experiments	13
Sampled, Real-time Diagnostics	13
Gas analyzers	13
Aerosol Spectrometer	16
Cascade Impactor	16
3. Coals and Coal Analyses	17
Coal Characterization: A Brief Overview	17
Standard Analyses	20
Total Sulfur and Sulfur in Ash	20
Chlorine	21
Ash	22
Advanced Analyses	22
Brief Summary of Principal Advanced Analyses	22
CCSEM	23
Instrumental and Sample Preparation Issues with CCSEM	23
Statistical Analysis of CCSEM	36
Overall Conclusions Regarding CCSEM Analyses	41

Chemical Fractionation.....	41
4. Transformations	51
Fly Ash Formation: A Brief Overview.....	51
Transformations of Representative Species	52
5. Deposit Formation.....	59
Ash Deposition: A Brief Overview	59
Mechanistic Description of Ash Deposition	60
Frame of Reference	60
Inertial Impaction $I(t, \tau)$	62
Thermophoresis $T(t, \tau)$	65
Condensation $C(t, \tau)$	67
Chemical Reaction $R(t, \tau)$	68
Eddy Impaction $E(t, \tau)$	69
Ash Deposition in Practical Systems	70
Utility Boiler (CIPS).....	70
Comparison of Experimental Results with Predictions.....	72
Qualitative Predictions and Observations	72
Quantitative Predictions and Experimental Results	73
Conclusions Regarding Deposit Formation Mechanisms	76
6. Particle Transport Equations.....	80
Particle Trajectories	80
Particle Energy (Heat) Transfer.....	83
Particle Reaction and Mass Transfer.....	85
Phase Changes.....	85
Fragmentation.....	87
Oxidation and Mass Transfer Rates.....	87
7. Deposition Mechanisms	92
Inertial Impaction $I(t, \tau)$	93
Capture Efficiency $G(t, \tau)$	105
Thermophoresis $T(t, \tau)$	108
Condensation $C(t, \tau)$	112
Reaction $R(t, \tau)$	114
Eddy Impaction $E(t, \tau)$	116
Other Mechanisms	117
Conclusions	118
8. Particles and Clouds.....	119
Conceptual Illustration of the STP Model.....	120
Theoretical Discussion	122
General Equations for the STP Model.....	124
Markovian Approximation	127

General Equations for the STP Model	123
Markovian Approximation	126
Fluid Particle (Gas) Dispersion	127
Parameter Definition for two-equation turbulence models	127
Comparison of Results with Analytical and Experimental Data	129
Implications for Particle Dispersion Generally	132
Conclusions Regarding Particle Concentration Profiles	134
9. Deposit Properties and Property Algorithm Development	135
Emissivity and Absorptivity of Deposits	135
Thermal Conductivity of Deposits	139
Deposit Strength, Tenacity, and Resistance to Thermal Shock	140
Ash Viscosity	140
Deposit Porosity	140
Results Illustrating the Impact of Thermal Properties on Boiler Performance	141
Conclusions Regarding Algorithms for Deposit Properties	147
10. Overall Conclusions	148
Coal Characterization	148
Fly Ash Generation	148
Ash Deposition	149
Deposit Properties	149
Final Conclusions	149
11. Acknowledgements	150
12. References	151
Appendix 1: Coal Characterization	160
Summary of Analysis Procedures	160
Proximate Analyses	164
Ultimate Analyses and Chlorine	165
Ash Chemistry	166
Heating Value	167
Forms of Sulfur	168
Ash Fusion Temperatures	169
Chemical Fractionation Data	171
Chemical Fractionation Procedure	175
Sample Preparation	175
Unleached Material	175

Ash Chemistry	176
Option of Analyzing Leachates in Addition to Solid Samples	177
Analysis of the Chemical Fractionation Procedure	180
Combination of Inorganic Transformations and Chemical Fractionation Data	185
<i>Appendix 2: Inorganic Transformations</i>	187
Thermochemical Equilibrium Predictions of Ash Deposit Chemistry	187
<i>Appendix 3: Deposit Properties</i>	192
Abstract	192
Introduction	192
Experimental Methods.....	194
Experimental facility.....	194
Experimental Procedure.....	194
Instrumentation.....	195
Data Interpretation.....	197
Results and Discussion	197
Surface temperature, deposit thickness, and heat flux measurements.....	197
Deposit thickness.....	198
Deposit and probe surface temperature.....	198
Heat flux	200
Deposit Thermal Conductivity.....	200
Experimental Uncertainty	201
Conclusions	203
Abstract	210
Introduction	210
Methods.....	211
Experimental Procedure.....	211
Theoretical Limits and the Structural Parameter	213
Results and Discussion	214
Measurements of Deposit Thermal Conductivity	214
Sintering and deposit microstructure	216
Sintering and Deposit Temperature	218
Sintering and deposit composition.....	218
Implications for Model Development.....	218
Conclusions	220
<i>Appendix 4. Publications</i>	228
<i>Appendix 5: Databases</i>	235

List of Figures

Figure 1	Artist's diagram of Sandia's Multifuel Combustor.	6
Figure 2	Schematic diagram of the Multifuel Combustor.	8
Figure 3	Schematic diagram of the temperature-controlled probe used to collect ash deposits on simulated convection pass surfaces.	9
Figure 4	Schematic diagram of the deposit topology diagnostic.	10
Figure 5	Quantitative spectral emissivities calculated from in situ FTIR emission spectra of deposits from two different coals forming on simulated heat transfer surfaces in the Multifuel Combustor.	11
Figure 6	Schematic diagram of the dynamic balance used to determine deposit mass accumulation.	12
Figure 7	Typical example of the array of experimental devices used in the MFC for deposit characterization. In this case, pyrometers, probes, laser range finder etc. are in the test section of the MFC.	13
Figure 8	Heating values (moist, mineral-matter-free basis) for the coals examined in this work.	18
Figure 9	Coalification diagram indicating the relationship between a variety of solid fuels in terms of their chemical composition. The labeled regions represent qualitative boundaries for different fuels. The points represent quantitative results of chemical analyses for various materials.	19
Figure 10	Typical CCSEM profile of mineral composition in the small size range.	24
Figure 11	Block diagram for CCSEM analysis of coal-derived samples.	26
Figure 12	Schematic diagram (a) and PRC image (b) illustrating the steps performed during grain recognition and characterization. The white nodes in the three examples in part (a) indicate bisection points and the solid nodes indicate the center as determined by the particle recognition and characterization software.	27
Figure 13	Illustration of (a) an SEI of Pd spheres, (b) the PRC image of the same sample, with X representing the location used to generate the waveform illustrated with its threshold (set at 69) indicated in (c), and (d) the actual and measured particle size distributions. Compare with Figure 14.	30
Figure 14	Illustration of (a) an SEI of Pd spheres, (b) the PRC image of the same sample, with X representing the location used to generate the waveform illustrated with its threshold (set at 82) indicated in (c), and (d) the actual and measured particle size distributions. Compare with Figure 13.	31
Figure 15	Illustration of PRC images of the Cu-Ta mixture in cross section with threshold levels at (a) 62, and (b) 96. The backscattered electron image (BEI) of the same sample is indicated in (c), and a comparison of the total number of particle counts in indicated in (d).	32
Figure 16	Similar to Figure 13(c) with arrows indicating distinctive aspects of wave forms produced around particles when secondary electron images (SEI) are used. Compare with Figure 17(c).	32
Figure 17	Illustration of the same sample as is used in Figure 13, Figure 14 and Figure 16, except that it is obtained as a backscattered electron image (BEI). Illustration of (a) the BEI of Pd spheres, (b) the PRC image of the same sample, with X representing the location used to generate the waveform illustrated with its threshold (set at 69) indicated in (c), and (d) the actual and measured particle size distributions. Compare (c) with Figure 16.	33
Figure 18	Illustration of (a) BEI of cross-sectioned Pd-Rh particles, (b) a waveform with accelerating voltage at 10 kV, (c) a wave form with accelerating voltage at 25 kV, and (d) a comparison of the measured particle size distributions.	34
Figure 19	Log-normal distributions with specified parameters, expected values, and standard deviations.	38
Figure 20	Same data as in Figure 19 plotted on a logarithmic scale, revealing the underlying shape of a normal distribution.	38
Figure 21	Results from chemical fractionation analyses of sodium as a function of coal rank for a suite of mostly US coals, with rank increasing from left to right.	47
Figure 22	Results from chemical fractionation analyses of potassium as a function of coal rank for a suite of mostly US coals, with rank increasing from left to right.	48
Figure 23	Major forms of inorganic material in a suite of US coals, arranged in rank order and by mineral class. See Table 7. Species are presented in the graph from bottom to top in the order indicated in the legend.	49
Figure 24	Major forms of inorganic material in coal as a function of coal rank as determined by chemical fractionation. Species are presented in the graph from bottom to top in the order indicated in the legend.	50

Figure 25	Modes of occurrence of inorganic material as a function of coal rank for US coals. Species are presented in the graph from top to bottom in the order indicated in the legend.	50
Figure 26	Schematic illustration of the fate of inorganic material in coals during combustion. Inorganic material in the raw coal may be atomically dispersed or in grains. The grains may be imbedded in the coal (as illustrated) or extraneous to it.	52
Figure 27	Thermal decomposition of hydrated calcium sulfate (gypsum) during particle heating.	54
Figure 28	Dehydration of gypsum to produce anhydrite with residual hydrated sulfate persisting to significant temperature.	54
Figure 29	Reactions of illite (represented here by muscovite) during rapid heating.	55
Figure 30	Kaolinite decomposition as a function of temperature.	56
Figure 31	Decomposition and oxidation of pyrite during typical combustion conditions.	56
Figure 32	Phase transformations of minerals commonly found in coal.	58
Figure 33	Conceptual illustration of inertial impaction mechanism on a cylinder in cross flow. One rebounding and one sticking particle are also illustrated.	62
Figure 34	Correlation of particle impaction efficiency on a tube in cross flow as a function of Stokes number. Points and functions designated R are from the literature [Israel and Rosner 1983; Baxter and Hardesty 1990].	64
Figure 35	Schematic illustration of thermophoretic deposition on a tube in cross flow.	65
Figure 36	Schematic illustration of condensation on a tube in cross flow.	66
Figure 37	Schematic illustration of chemical reaction on a tube in cross flow.	68
Figure 38	A cross-sectional view of the CIPS 600 MW _e unit used in performing a test burn of the Wyoming coal. Circles indicate locations from which ash deposits were sampled after the test burn.	70
Figure 39	Comparison of sensitivity of data (symbols) and predictions (lines) to particle residence time for a Pittsburgh #8 coal. The dominant dependence in this particular case is the iron concentration. Data are from the MFC.	73
Figure 40	Deposit viscosity predicted from measured, predicted, and coal ash composition for the Pittsburgh #8 coal at 0.2 s residence time in the MFC. A notable improvement in the prediction is noted compared with the coal ash values.	74
Figure 41	Comparison of predicted and measured deposit compositions near the boiler nose in the CIPS 600 MW _e utility boiler. Replicated experiments in this facility indicate a standard deviation of the data of less than eight relative percent for all oxide species.	76
Figure 42	Comparison of predicted and measured deposit compositions on economizer tubes in the CIPS 600 MW _e utility boiler.	76
Figure 43	Comparison of deposit viscosity as a function of temperature in the first superheater tube bank over the nose in the 600 MW _e CIPS boiler.	77
Figure 44	Comparison of deposit viscosity as a function of temperature in the economizer of the 600 MW _e CIPS boiler.	77
Figure 45	Comparison of literature data and correlations for the drag coefficient over the range of interest in this project.	80
Figure 46	Conceptual illustration of inertial impaction mechanism on a cylinder in cross flow. The deposit is typically confined to the leading edge $\pm 50^\circ$ of the cylinder. Two particles are also illustrated, one which rebounds and one which sticks.	93
Figure 47	Schematic diagram of coordinate system and reference frames used in describing a tube in cross flow.	94
Figure 48	Illustration of particle streak lines and definition of particle impaction efficiency for a cylinder in cross flow.	95
Figure 49	Theoretical calculation of particle impaction efficiencies as a function of particle size at three levels of sophistication.	96
Figure 50	Predicted particle impaction efficiency (expressed as a percent) as a function of angular position measured from the leading edge of a cylinder in cross flow.	97
Figure 51	Sensitivity of particle impaction efficiency to turbulent fluctuations in the gas and particle velocity. A Gaussian distribution of velocity fluctuations was assumed in making these predictions.	99

Figure 52	Sensitivity of particle impaction efficiency on a tube in cross flow to turbulent fluctuations in gas and particle velocity. A (skewed) Rayleigh distribution of velocities was assumed in making these predictions.....	100
Figure 53	Correlation of particle impaction efficiency as a function of Stokes number. Points are from our calculations. Original function is from the literature [Israel and Rosner 1983]. Modified (and original) function parameters are presented in Table 9.....	101
Figure 54	The predicted impaction efficiency of particles on flat plates as a function of particle Stokes number.....	103
Figure 55	Illustration of the impact of using the velocity mean rather than median in the Stokes number calculation for flat plates. Also shown for comparison are the correlations for the cylinder in cross flow (divided by 2) and for the flat plate.....	105
Figure 56	Illustration of the parameters and form of the correlating expression used to describe particle capture efficiencies for both tubes in cross flow and flat plates.....	106
Figure 57	Schematic illustration of thermophoretic deposition on a tube in cross flow.....	107
Figure 58	Predicted thermophoretic force as a function of particle size using several different models.....	110
Figure 59	Predicted thermophoretic force as a function of Knudsen number over the range of particle sizes of importance in pulverized coal combustion.....	111
Figure 60	Schematic illustration of deposition by condensation on a tube in cross flow.....	112
Figure 61	Schematic illustration of chemical reaction on a tube in cross flow.....	114
Figure 62	Illustration of the condensation of (potassium) chloride in the case of wheat straw combustion and the subsequent reaction of the chloride to form a sulfate when wheat straw and coal are cofired, leading to a significant decrease in corrosion rates.....	115
Figure 63	Illustration of the discrepancy between the thermophoretic driving force and the observed rate of deposition of submicron particles on a simulated heat transfer surface under commercial conditions.....	116
Figure 64	Illustration of the development of a Lagrangian pdf for particle position in an arbitrary coordinate system. At short residence times the mean particle location is near the point of injection (the origin in this case) as represented by the peak in the particle position pdf. The pdf is confined to a relatively small region of the flow domain. Flow is directed primarily in the + x direction. Compare with Figure 65 and Figure 66.....	120
Figure 65	Illustration of the development of a Lagrangian pdf in an arbitrary coordinate system. At intermediate residence times the mean particle location is in a central region in the flow domain and the particle position pdf has nonzero values in a significant region of the flow domain. Compare with Figure 64 and Figure 66.....	120
Figure 66	Illustration of the development of a Lagrangian pdf in an arbitrary coordinate system. At long residence times the mean particle location approaches the exit of the flow domain (flow is directed primarily in the + x direction) and the particle position pdf has nonzero values over most of the flow domain. Compare with Figure 64 and Figure 65.....	121
Figure 67	A Lagrangian view of dispersion in a one dimensional flow. Each circle is a measure of the spatial extent of a pdf for particle position at successive times during the flow. The position of a typical Eulerian computational cell is also illustrated. Particles of many different residence times contribute to the overall population of particles in the cell.....	122
Figure 68	Comparison among several particle dispersion models and an analytical solution.....	129
Figure 69	Comparison of fluid particle dispersion exhibiting Markovian-type dispersion. The diffusion coefficient is proportional to the slope of the data and clearly time dependent.....	131
Figure 70	Comparison of particle autocorrelation functions, normalized by measured integral scales, and the Markovian autocorrelation. The diffusion coefficient is residence time dependent until the autocorrelation function becomes identically zero.....	132
Figure 71	Illustration of the behavior of a diffusion coefficient based on a Markovian process and the diffusion coefficient from more complicated flows, in this case exhibiting counter-gradient diffusion.....	133
Figure 72	Illustration of the significance of a time dependent diffusion coefficient in making Eulerian calculations of particle dispersion. Identical particles in identical environments exhibit different diffusion coefficients at the same location because of the residence-time dependence of the correlation functions.....	133
Figure 73	Schematic illustration of the solution of the radiative transport equation.....	136

Figure 74	Illustration of the bi-directional reflectance as a function of angle of incident light for particles of significantly different scattering properties. The peak illustrated at about 1 radian is associated with an intense back scatter from granulated material known as the opposition effect.	138
Figure 75	Parametric variation of deposit temperature as a function of position for various values of the solid volume fraction and tortuosity. See text for details of incident heat flux, etc.....	143
Figure 76	Deposit surface temperature and heat flux as a function of porosity and emissivity assuming no intra-deposit radiative heat transfer and a non-conducting gas phase. Tortuosity is assumed to be unity. .	143
Figure 77	Deposit surface temperature and heat flux under the same assumptions as in Figure 76 but assuming a linear relationship between emissivity and porosity.	144
Figure 78	Conceptual illustration of the changes in contacting efficiency and tortuosity with sintering/melting.	145
Figure 79	Change in porosity and apparent density with time for an Illinois #6 coal ash accumulating on a tube in cross flow.	145
Figure 80	Measured and theoretical development of thermal conductivity in an ash deposit formed in the Multifuel Combustor.	146
Figure 81	Measured development of thermal conductivity in an ash deposit from a Black Thunder coal.	147
Figure 82	Schematic illustration of the chemical fractionation procedure.	178
Figure 83	Logic diagram for the chemical fractionation procedure.	179
Figure 84	Consistency of the silicon tracer technique in determining residual mass during the water leaching step of the chemical fractionation procedure. The results are inversely related to the percent loss of silicon. Less than 0.01 percent of the silicon was removed in this step. Contrast with Figure 85 and Figure 86.	180
Figure 85	Consistency of the silicon tracer technique in determining residual mass during the ammonium acetate leaching step of the chemical fractionation procedure. The results are inversely related to the percent loss of silicon. Less than 1 percent of the silicon was removed in this step. Contrast with Figure 84 and Figure 86.	181
Figure 86	Consistency of the silicon tracer technique in determining residual mass during the hydrochloric acid leaching step of the chemical fractionation procedure. The results are inversely related to the percent loss of silicon. Less than 10 percent of the silicon was removed in this step. Contrast with Figure 84 and Figure 85.	182
Figure 87	Comparison between the elemental composition of the water leachate as analyzed and as calculated based on the solids analysis for the Wyodak coal. Compare with Figure 88 and Figure 89.	183
Figure 88	Comparison between the elemental composition of the ammonium acetate leachate as analyzed and as calculated based on the solids analysis for the Wyodak coal. Compare with Figure 87 and Figure 89.	184
Figure 89	Comparison between the elemental composition of the hydrochloric acid leachate as analyzed and as calculated based on the solids analysis for the Wyodak coal. Compare with Figure 87 and Figure 88.	185
Figure 90	Atomically dispersed titanium as determined from the chemical fractionation technique compared with the amount of titanium lost during devolatilization for many of the suite of coals studied in the MFC.	186
Figure 91	Moles of a variety of potassium-containing compounds as a function of temperature as predicted by a commercial thermochemical equilibrium code.	188
Figure 92	Predicted heat capacities of K-feldspar and several of its isomers as derived from a commercial database. The two species designated K and X behave in a manner inconsistent with physical chemistry.	189
Figure 93	Predicted heat capacities of K-feldspar and several of its isomers after correction of the sign on one coefficient for each of the two odd-behaving species.	190
Figure 94	Predicted equilibrium composition of potassium-containing species under the same conditions as Figure 91 but with the spurious data removed from the database. This figure is plotted on the same scale as Figure 91. See Figure 95 for a more detailed view (larger scale).	191
Figure 95	Predicted equilibrium composition of potassium-containing species under the same conditions as Figure 91 but with the spurious data removed from the database. See Figure 94 for legend.	191
Figure 96	Schematic of Multifuel Combustor.	204

- Figure 97 Details of the probe in the experimental set-up in the test section of the Multifuel Combustor (set up is illustrated in Figure 7). Neither figure is drawn precisely to-scale, but each provides a reasonable representation of the probes and instrumentation used for these experiments. 205
- Figure 98 Time-resolved measurements: a) average deposit thickness, b) average probe and deposit surface temperatures, and c) heat transfer rate through the test section. The open circles in (c) represent the uncorrected deposit surface temperature, as described in the text. 206
- Figure 99 Deposit thickness measurements made with the range-finding laser system. As described in the text, the baseline representing the probe surface has been subtracted off these measurements. The labels indicate the elapsed experimental time when the scan was taken. For visual clarity, results from only three scans taken along the same probe orientation are shown. The axial location is determined by the position-encoded bearing and does not correspond to the distance across the reactor. 207
- Figure 100 Ten minutes of probe and deposit surface temperature measurements. The numbers on the figure indicate the angle between the pyrometer focal volume and the leading edge of the probe. The vertical lines indicate approximately when the shifts in pyrometer orientation occurred. The pyrometer data have been corrected for deposit emissivity and reflected radiation. For visual clarity, measurements from two of the four probe surface temperature thermocouples and one of the three optical pyrometers are not shown. 207
- Figure 101 Probe and deposit surface temperature as a function of azimuthal angle θ . The temperature at the leading edge of the probe corresponds to 0° ; a plane of symmetry exists along a vertical line drawn between 0° and 180° . The solid line indicates a least-squares fit ($r^2 = 0.98$) of a sinusoid to the average deposit surface temperature measurements made at each angular orientation, which are indicated by the open circles. The vertical bars indicate the uncertainty on deposit surface temperature measurement. 208
- Figure 102 Time-resolved measurements of the thermal conductivity of several deposits formed while firing a 65/35% (by mass) blend of Illinois #6 coal and wheat straw. The measurements indicated by the open circles correspond to the data presented in Figure 98 through Figure 101. The vertical error bars indicate the maximum experimental uncertainty of $\pm 20\%$, and are only shown one set of experimental data for visual clarity. 208
- Figure 103 a) Average probe surface temperature, and b) probe surface temperature gradient as a function of axial distance. The vertical dashed lines indicate the 50-mm-wide temperature window and the vertical solid lines indicate the optimum placement of the 35-mm-wide deposit test section within this window. The edges of the reactor tube correspond to 0 and 150 mm. The direction of cooling air flow is from left to right in this figure. 209
- Figure 104 Measurements of (a) average deposit thickness, (b) average probe and deposit surface temperature, and (c) deposit solid fraction, (d) deposit structural parameter, and (e) deposit effective thermal conductivity as a function of time. This deposit was created while firing the blend of Illinois #6 and wheat straw. Figure (e) also compares the measured values to theoretical limits for deposit thermal conductivity. The thick vertical line indicates the transition between the growth and sintering phases of the experiment. Vertical bars in (e) indicate estimate of experimental uncertainty. 222
- Figure 105 Thermal conductivity measurements and theoretical limits as a function of deposit solid fraction. Data are from the same experiment as those shown in Figure 104. Vertical bars show estimate of experimental uncertainty on selected data points. Time increases from left to right, but note that solid fraction does increase linearly with time as shown in Figure 104c. 223
- Figure 106 Measurements of (a) deposit solid fraction, and (b) deposit effective thermal conductivity as a function of time. As described in the text, these measurements were conducted under the same experimental conditions, but the experiments were terminated after different periods of sintering to examine the changes in deposit microstructure. The vertical line at 0 hours elapsed time indicates the start of sintering portion of the experiment. Data for the deposit sintered for 12 hrs are also shown in Figure 104 and Figure 105. The theoretical limits are calculated from the solid fraction of the deposit sintered for 12 hrs. The elapsed time for some of the thermal conductivity measurements has been slightly shifted for visual clarity. Vertical bars indicate estimate of experimental uncertainty on selected data points. 224
- Figure 107 Electron micrographs of cross-sections of an unsintered deposit and a deposit sintered for 12 hours impregnated in epoxy. The bright regions in these images correspond to cross-sectional profiles of

	<i>deposit solid phase material; the dark regions correspond to void space. The entire cross-section of the sintered deposit and part of the cross section of the unsintered deposit is shown in the figure.....</i>	<i>225</i>
Figure 108	<i>Electron micrographs of the inside and outside surface of deposits that have been sintered for 0, 1, 4, and 10 hours. These deposit samples were directly carbon coated and analyzed with the SEM, as described in the text.</i>	<i>226</i>
Figure 109	<i>Calculations of the overall deposit thermal conductivity with the two-layered structure model as a function of the thermal conductivity of the sintered layer, k_{si}. Curves are shown for three different values of the nondimensional thickness of the unsintered layer, L, and a constant value of the unsintered layer, k_{un}.</i>	<i>227</i>
Figure 110	<i>Comparison of the measurements of deposit thermal conductivity shown in Figure 1e to predictions of the two-layered structure model as a function of time. The values of k_{un}, k_{si} and L used to evaluate the model are described in the text. Elapsed time corresponds to the sintering stage of the experiment. Vertical bars indicate estimate of experimental uncertainty on selected data points.</i>	<i>227</i>

List of Tables

Table 1	Summary of on-line gas analysis systems, techniques, and ranges routinely used in the MFC.....	14
Table 2	Summary of interferences between various gas measurements in the MFC gas analysis systems.....	14
Table 3	Summary of on-line gas analysis systems, techniques, and ranges routinely used in the MFC.....	15
Table 4	Summary of interferences between various gas measurements in the portable gas analysis systems.	16
Table 5	Experimental Parameters for the Investigation of the Effects of Instrument Parameters and Sample Preparation on CCSEM Results.....	28
Table 6	Experimental Design for the Investigation of the Effects of Instrument Parameters and Sample Preparation on CCSEM Results.....	29
Table 7	Major compounds in each of the classes indicated in Figure 23.....	42
Table 8	Mineral groups, names, formulas, and characteristics of commonly occurring minerals in coal.....	43
Table 9	Elemental ratios and solubilities of major inorganic species found in coal.	45
Table 10	Parameters for the correlation describing the Reynolds number dependence of the particle drag coefficient (see Eq.(19)).	81
Table 11	Original and Modified Coefficients in the Correlating Expression for Particle Impaction Efficiency on Cylinders in Cross Flow.....	102
Table 12	Coal-related standards published standards under the jurisdiction of the Methods of Analysis Subcommittee (D05.21) of the ASTM.....	161
Table 13	Coal-related standards published standards under the jurisdiction of the Major Elements in Ash and Trace Elements of Coal Subcommittee (D05.29) of the ASTM.	162
Table 14	Summary of Standards for Analytical Procedures.....	163
Table 15	Summary of Proximate Analysis data for a suite of US coals.....	164
Table 16	Summary of Ultimate Analysis Data for a Suite of US Coals	165
Table 17	Summary of Ash Chemistry Data for a Suite of US coals.	166
Table 18	Summary of Heating Values for a Suite of US Coals.....	167
Table 19	Summary of Forms of Sulfur Analyses for a Suite of US Coals.	168
Table 20	Summary of Ash Fusion Temperatures Data for a Suite of US Coals.....	169
Table 21	Summary of water soluble fractions from chemical fractionation data for a suite of coals.	171
Table 22	Summary of ion exchangeable fractions from chemical fractionation data for a suite of coals.....	172
Table 23	Summary of acid soluble fractions from chemical fractionation data for a suite of coals.....	173
Table 24	Summary of residual fractions from chemical fractionation data for a suite of coals.....	174
Table 25	Measurement uncertainties.....	201
Table 26	Selected results from standard analysis of fuel and ash samples. The sintered deposit sample was sintered for 4 hours.....	212

Executive Summary

This report summarizes experimental and theoretical work performed at Sandia's Combustion Research Facility (CRF) over the past eight years, on the fate of inorganic material during coal combustion. The work was sponsored by the Department of Energy's Office of Fossil Energy, Coal Utilization Advanced Research Program through the National Energy Technology Laboratory (formerly FETC and PETC).

The work has been lead by Sandia's principal investigator Dr. Larry Baxter, with significant contributions over the years by many others, including other Sandia staff, technologists, post docs, visitors and students (see the Acknowledgements, Section 11). We want to expressly acknowledge the expertise and essential contributions of Gian Sclipa, Sandia Principal Technologist, to all aspects of the experimental work. The FE program manager is Philip Goldberg (NETL). Don Hardesty is the Sandia project manager. During the period of performance, Sandia has documented the work in regular Quarterly Reports, submitted to the FE program manager and available for wide distribution. The most significant aspects of the work have been presented to the technical community at meetings, conferences, and symposia, and are published in the technical literature (see the comprehensive list of publications in Appendix 4).

This work has been done under four broad categories: coal characterization, fly ash formation, ash deposition, and deposit property development. The objective of the work was to provide sufficient understanding of these four areas to be able to predict coal behavior in current and advanced conversion systems. We take quantitative prediction as the standard of sufficient understanding, and this document includes the quantitative expressions for describing inorganic behavior in each of these areas. To avoid obscuring the concepts by developing the quantitative details, we sometimes summarize the conceptual information first and then develop a detailed description.

Prior to the discussion of these four major topics, we summarize the experimental facilities used in these investigations. Nearly all of the experimental data reported in this document derives from the Multifuel Combustor (MFC) Laboratory at Sandia. Much of the instrumentation used to develop these data was developed as part of this research effort. The capabilities of the facility and the accuracy and precision of its major components are summarized.

As part of the discussion of the fuel characterization, we introduce a suite of over 30 coals that form the basis of the experiments used in this investigation. These fuels span the range of lignites to lv bituminous coals, but primarily focus on subbituminous and hv bituminous coals of commercial significance. The report summarizes a few essential characteristics of these fuels, with the complete fuel analyses being placed in the Appendix.

The general discussion is organized into the following major subjects: introduction; fuel characterization; fly ash formation and fuel reactions; deposition mechanisms; deposit properties; and integrated descriptions of deposit formation. The current understanding and critical unresolved issues are summarized within each of these major topic areas. Quantitative analysis

tools and algorithms describing the data are also described in substantial detail. In addition to this general discussion, there are three topics specific to the results of this report. These include a discussion of the experimental equipment used in these analyses, a discussion of the suite of coals used in the experimental investigations, and a discussion of a turbulent particle modeling approach that forms the basis of the integrated description of the ash deposition model. Appendixes record some of the more detailed information in many topic areas.

Fuel Characterization

The major means of characterizing inorganic material in fuels are briefly summarized. The greatest contribution of this work is the development of a repeatable technique for transforming inorganic elemental information available from standard fuel analyses into quantitative, species-specific information about the inorganic materials. This technique is based largely on standardized analyses and the chemical fractionation analysis. Chemical fractionation has been used for many years to characterize fuels, but we are not aware that it has been as systematically analyzed or as fully developed to characterize inorganic species in fuels as is done in this work. The primary result of this work is the presentation of a methodology for characterizing the inorganic fractions of fuel and results from applying this methodology for a wide range of coals. These results provide sufficient detail about fuel chemistry to support the remaining tasks. There remain several unresolved issues in this characterization, but in general terms, fuel characterization is more advanced than the other tasks and requires less development work. Fuel characterization techniques are no longer a critical path item with regard to improving our understanding of the fate of inorganic material during combustion. The single critical aspect of fuel characterization needing more research is the establishment of standards with which to compare the various species-specific analyses.

Fly Ash Generation

Fly ash generation focuses on the transformations that occur as fuel particles react to form fly ash. In this document, the species indicated from the fuel characterization work undergo separate and specific transformations. These are summarized and illustrated for most of the major species that occur in fuel. In earlier work, we developed several important mechanisms of fly ash transformation that are used but not significantly discussed in this report. These include rates and extents of char fragmentation and mechanisms of inorganic release from reacting fuel particles.

There remain several critical issues in describing fly ash transformation. These include specification of thermodynamic and kinetic parameters for the species, descriptions of interactions between species during particle combustion, and description of transport processes limiting such interaction (diffusion coefficients) or resulting from such interactions (viscosity). These issues are approximated in this document, but in general require additional research for better characterization.

Ash Deposition

The mechanisms and rates of ash deposit formation are discussed in detail. The major mechanisms are summarized and quantitative expressions of their rates are compared. The most important deposition mechanisms are identified and are accurately characterized. The amount of

material deposited by a given mechanism and the influence of that material on deposit properties are both regarded as measures of importance. Less important, but non-negligible deposition mechanisms are also discussed. This document highlights both the agreement and disagreement of several mechanisms with data and theory. Resolution of some of the remaining disagreements between various theories and data remains a critical-path issue in understanding the fate of inorganic material in combustors. However, the mechanisms responsible for most of the mass of deposition are reasonably well characterized.

Deposit Properties

One of the primary focuses of this work in the last several years has been experimental and theoretical analysis of deposit properties. Several major contributions have been made in this regard. For the first time, critical deposit properties such as thermal conductivity, emissivity, strength, etc. have been placed on a firm theoretical foundation. Experimental diagnostics and techniques have been developed for characterizing these properties under realistic combustion conditions. Comparisons of experimental data and theory have resolved some previously confusing results and have led to new disagreements with theory in other areas. Deposit properties remain possibly the single most critical issue to be resolved in describing the fate of inorganic material during combustion.

Overall Conclusions

This work has led to new characterization techniques for fuels that provide, for the first time, systematic and species specific information regarding the inorganic material. The transformations of inorganic material during combustion can be described in terms of the net effects of the transformations of these individual species. Deposit formation mechanisms provide a framework for predicting deposition rates for a broad range of particle sizes. Predictions based on these rates many times are quite accurate, although there are important exceptions. A rigorous framework for evaluating deposit properties (thermal conductivity, emissivity, strength, etc.) has been established as a result of this work. Substantial data have been obtained with which to exercise this framework, but this portion of the work is less mature than is any other. Accurate prediction of deposit properties as functions of fuel properties, boiler design, and boiler operating conditions represents the single most critical area where additional research is needed.

1. Introduction

Among the issues that determine the design and operation of coal utilization equipment, ash deposition on combustor surfaces plays a significant, in many cases dominant, role. A brief survey of the development of coal conversion technologies identifies the historical role of ash deposition as a motivation for major new technologies and concludes that "it is ... inevitable that there will be always some problems with ash, whatever the system of coal combustion" [Raask 1984]. Nevertheless, the fate of inorganic material during combustion remains less well understood than the combustion of the organic material. While there are several indices of ash behavior, there is no complete model that describes ash deposition in a comprehensive way. This report describes progress toward development and validation of such a model.

The impact of ash deposition on pulverized coal (pc) boiler operation and design and on fuel selection is not difficult to establish. One vivid illustration is the comparison of the size of boiler required to produce the same amount of electrical power from low-rank and high-rank coals. Typically, a boiler designed for combustion of subbituminous coals is about 40% taller and 20% wider and deeper than a similarly rated boiler designed for bituminous coal. This increase in size is required even though the low rank fuel combusts notably faster than the high rank fuel. The primary reason for the increase in size is to accommodate differences in the behaviors of the inorganic material associated with these two coals, specifically the properties of the ash deposits that they form. The increased surface area in the boiler for the low-rank fuel allows the operator to manage this ash behavior without compromising boiler lifetime or damaging boiler components.

Ash issues are further complicated by current trends among utility power generators in both the US and abroad. In the past, boilers largely burned fuels supplied by local or regional mines under long-term contracts. A combination of environmental pressures and deregulation has created much larger variation in the fuels being used by boilers and has led to widespread fuel blending. In the past, long-term experience with a single or small number of coals partially compensated for an inability to quantitatively anticipate the behavior of the inorganic material in these coals. The wide variation in fuels currently being used in coal boilers does not allow for operator experience to compensate for lack of adequate predictive tools.

In general, ash behavior depends on fuel properties, boiler design, and boiler operation. Industrial practice has led to the development of a wide variety of indices, nearly all of which are based entirely on fuel properties, for predicting ash behavior. These include arithmetic combinations of elemental mass fractions in the ash, fusion temperatures, slag viscosity-related measurements, etc. It is on the basis of these parameters that the coal-fired electrical power industry has developed a large, stable, reliable suite of boilers. This achievement deserves a measure of respect. However, these indicators of ash behavior are universally recognized as marginally accurate. There is a critical need for improved accuracy, given the combination of the effect of ash on boiler performance and current market trends leading to increased variation and generally decreased quality of coals used in most boilers.

There are several areas in which these indices could be improved. Very few of the indices include boiler design or operation information even though it is clear that any coal can induce serious deposition problems in any boiler if the boiler is improperly operated or designed inappropriately for that fuel. Furthermore, it is common that the deposits formed in boilers have quite different composition than the inorganic material in the fuel, due to some highly selective deposition processes. Additionally, none of the traditional analyses differentiate different chemical forms of the inorganic material at a level beyond their elemental composition. Information on the chemical form of the inorganic material, for example pyrite vs. siderite, is essential to understanding its combustion behavior. Additional information that is useful in understanding ash deposition is the coal-particle-to-coal-particle variation in inorganic material, the amount of excluded inorganic material, and the size and shape of the mineral grains. Since none of this information is typically included in traditional standardized analyses or indices, the marginal accuracy of the indices is understandable.

This report is organized into the following major Sections: (1) Introduction, (2) Experimental Equipment, (3) Coal and Coal Analyses, (4) Transformations, (5) Deposit Formation, (6) Particle Transport Equations, (7) Deposition Mechanisms, (8) Particles and Clouds, (9) Deposit Properties and Property Algorithm Development, (10) Overall Conclusions (11) Acknowledgements, (12) References, and (13) Appendices. The current understanding and critical unresolved issues are summarized within each topical area. Quantitative analysis tools and algorithms describing the data are also described in substantial detail. In addition to these general discussions, there are three topics specific to the results of this report. These include a discussion of the experimental equipment used in these analyses, a discussion of the suite of coals used in the experimental investigations, and a discussion of a turbulent particle modeling approach that forms the basis of the integrated description of the ash deposition model. Appendixes record more detailed information in many topic areas, including a detailed summary of data for each of the coals that was examined.

2. Experimental Equipment

In this section we review the experimental facilities, probes, diagnostics, and fuels used in this investigation. The experimental facilities include the Multifuel Combustor at Sandia National Laboratories' Combustion Research Facility (CRF) in Livermore, CA, and its associated diagnostics. Temperature-controlled probes are used to simulate the heat transfer tubes found in full-scale boilers. The probes are scaled with respect to Reynolds number, Stokes number, or both, depending on the particle deposition mechanisms under investigation. A variety of *in situ*, *ex situ* and *post mortem* diagnostics are used to characterize deposit properties on these surfaces. Those most relevant to this investigation are briefly presented here in the order of: (1) *in situ*, real-time, diagnostics; (2) sampling (*ex situ*), real-time diagnostics; and (3) sampling, *post mortem* diagnostics.

The Multifuel Combustor

The experimental work summarized in this report was principally conducted in the Multifuel Combustor (MFC).

Figure 1 Artist's diagram of Sandia's Multifuel Combustor.

The MFC is a small, pilot-scale (~40 kW, depending on coal type), down-fired, turbulent flow combustor, that is capable of firing a wide variety of fuels under diverse conditions of residence time, gas temperature, gas composition, etc. [Baxter 1992]. The MFC includes a commercial-style gas burner (see Figure 1 and Figure 2). The natural gas flame in this burner has roughly 200 ms of residence time before it enters the first module of the MFC. Alternatively, air can be electrically preheated in this section of the combustor, avoiding generation of a vitiated gas but limiting the preheat temperature to about 600 °C.

Fuel and oxidizer injection lances can be inserted at 11 axial locations in the combustor at any of four ports per axial location, for a total of 44 injection ports. Fuel residence time varies with the total gas flow rate and the point of fuel injection. The nominal fuel residence time in the MFC ranges from a few milliseconds to about five seconds. Smaller ports for insertion of diagnostic probes are also provided at 7 axial locations.

Below the electrical/gas burner preheating section, the MFC comprises seven modular sections with independently controllable wall temperatures. The wall temperatures range up to 1400 °C in each section. Gas temperatures can be either above or below the wall temperatures, depending on reaction conditions, initial gas temperature, and gas velocity.

The effluent from the series of modular sections passes through an instrument table on which are mounted a variety of diagnostics for probing gas, particle, and surface conditions. These diagnostics are described in more detail later. The approximate 35 cm tall region below the modular sections, at or above the instrument table, is referred to as the test section. Most of the detailed measurements are made in this region. The region offers essentially unobstructed optical and probe access to the particle-laden flow and to simulated heat transfer surfaces placed in the flow at this location. From this region, the flow and a sizeable amount of room air (nominally 100 to 1 dilution), enter an exhaust duct which eventually leads to a roof stack.

Multiple fuel and air lances allow a wide variety of conditions to be simulated in the MFC. Fuel staging, reburning, normal combustion, and a variety of other configurations have been simulated in the combustor. Additionally, a wide variety of fuels, including solids, suspensions, liquids, and gases, are routinely used in MFC investigations.

In Situ, Real-time Diagnostics

The *in situ*, real-time diagnostics used in this investigation monitor deposit and entrained particle properties. Monitored deposit properties include thickness, surface temperature, mass, and emissivity. Monitored entrained particle properties include number concentration, size distribution, and velocity. Deposition targets used in the test section of the combustor provide surfaces on which measurements are made. The probes also independently monitor properties such as heat flux, probe surface temperature, cooling gas flow rate, and cooling gas temperature. The deposition targets are discussed first, followed by discussions of the other *in situ*, real-time diagnostics relevant to this investigation.

Figure 2 Schematic diagram of the Multifuel Combustor.

Temperature-Controlled probes

Figure 3 illustrates the design of one-type of temperature-controlled target used to collect ash deposits in the test section of the MFC. The surface temperature of the probe is held constant through the use of thermocouples embedded in the surface, internal air-cooling, and a feedback control loop. The probes are capable of axial rotation to generate axi-symmetric deposits that are much easier to analyze for purposes of determining thermal conductivities, etc. Most typically, the probes were not rotated during these investigations. Many different probes of similar nominal design are used. Additional details of the designs include removable center sections to allow potting and subsequent microscopic analysis of the deposits, screens to promote uniform, turbulent plug flow through the sections used for heat transfer analysis, in-line heaters to allow greater temperature control, and insulation blocks to prevent lateral heat transfer.

Figure 3 Schematic diagram of the temperature-controlled probe used to collect ash deposits on simulated convection pass surfaces.

Laser Triangulation Diagnostic

A pulsed infrared laser mounted on a precision bearing measures surface topology and, by difference, deposit thickness along a single line parallel to the probe axis (Figure 4). The measurement range is 0-32 mm, and the resolution is $\pm 8 \mu\text{m}$ under ideal conditions, and $\pm 30 \mu\text{m}$ under typical combustion conditions. Successive scans along the same line at regular time intervals resolve the temporal growth rate of the ash deposit. A series of scans at different radial positions resolves spatial variations. When the deposit growth rate is small, signal-to-noise ratios are poor. Under these conditions, as were experienced during some of the fume deposition experiments, the deposit thickness could not be reliably resolved *in situ* even after several hours of growth.

Figure 4 Schematic diagram of the deposit topology diagnostic.

Optical Pyrometers

Optical pyrometers are used to measure deposit surface temperature and emissivity. The measurement technique assumes that all radiation in the instrument line of sight derives from surface emission. Therefore, measurements are made on the shadowed side of the probe with the deposit rotated out of the direction of flow of the gases to avoid surface reflections of flame radiation, or on the windward side with radiation temporarily blocked by some means.

Combustion flows with high particulate loading, such as those commonly experienced in commercial systems, require that the particles in the line of sight be blocked to prevent scattering of radiation into the pyrometers. Pyrometer temperature ranges of 250-850 °C and (400) - 1200 °C, respectively, exhibit an ideal accuracy of ± 0.25 °C and a practical accuracy of ± 1 °C in the absence of systematic errors, such as reflected or scattered radiation and variations in probe surface emissivity. Over the range of reasonable emissivities for such deposits, the temperature can be characterized within ± 15 °C. Deposits exhibit traditional geometries, as illustrated discussed later, or grow axisymmetrically. Axi-symmetric geometries result from rotating the probe at < 1 rpm along its axis. Such deposits simplify characterization of thermal conductivities whereas traditional deposits assist investigation of accumulation rates, structures, and growth mechanisms.

Fourier Transform Infrared Spectrometer

Fourier transform infrared (FTIR) emission spectroscopy is used to characterize spectral radiative properties and composition of the deposit. Spectral emissivities are characterized between 2.5 and 25 μm (4000 to 400 cm^{-1}) except in isolated bands where gas-phase, infrared-active species (principally H_2O and CO_2) interfere. Spectral emissivities can be determined within ± 5 percent.

Condensed-phase chemical species with identifiable signatures in this wavelength region are qualitatively identified. With respect to species of interest to combustion, this includes essentially all carbonates, sulfates, silicates, some oxides, but few chlorides. An example of several such *in situ* spectra collected during coal combustion is indicated in Figure 5.

Figure 5 Quantitative spectral emissivities calculated from *in situ* FTIR emission spectra of deposits from two different coals forming on simulated heat transfer surfaces in the Multifuel Combustor.

Differences in the shape of the spectra are indicative of different chemical compositions on the surface of the probe. Analysis of these differences is discussed later in this document.

Particle Counter, Sizer, Velocimeter

An *in situ*, laser-based diagnostic (PCSV system by Insitec, now Process Metrix) measures the particle concentration, size distribution, and velocity in the size range of 2-130 μm ideally, and 5-100 μm under most conditions relevant to commercial combustion. The device is a multibeam system that approximates a point measurement with diagnostic volumes approximately ellipsoidal in shape. The ellipsoidal diagnostic volumes have major and minor axes of about 1 mm and 450 μm for one beam and 0.3 mm and 50 μm for the second beam. The accuracy of the

diagnostic, when properly calibrated and aligned, is $\pm 10\%$ or $\pm 1 \mu\text{m}$, whichever is larger. Concentrations and velocities are measured with about $\pm 5\%$ accuracy. These accuracies are determined by spinning reticules with known particle sizes through the beam. Real systems typical of commercial combustion contain high particle loadings. This compromises the measurement by both beam obscuration and multiple scattering in the diagnostic volume such that data reliability for small particles ($< 5 \mu\text{m}$) degrades quickly. This investigation includes particles ranging in size from < 0.1 to $50 \mu\text{m}$. The smaller particle concentrations are measured using an aerosol spectrometer (discussed later).

Dynamic Balance

A magnetic force restoration dynamic balance characterizes deposit mass on a cantilevered probe (see Figure 6). The ideal resolution of the balance is $\pm 10\text{mg}$. When the deposit mass accumulation rate is small, instrumental drift becomes a major source of error in the measurements. Under such conditions, as are commonly experienced during slow deposition experiments, the mass of the deposit could not reliably be resolved *in situ*, even after several hours of growth. For the low-mass cases, the deposit is generally removed and weighed on an analytical balance. This provides only a single measurement of mass as opposed to the continuous measurements obtained from the dynamic balance.

Figure 6 Schematic diagram of the dynamic balance used to determine deposit mass accumulation.

Integrated Experiments

The collection of diagnostics used to characterize deposition rates and properties and their use in the MFC in a typical experiment are schematically illustrated in Figure 7. The details of this experiment are discussed later. Here we use the schematic diagram to illustrate the configuration of a typical deposition experiment. Only the last section of the MFC is indicated in this diagram.

Figure 7 Typical example of the array of experimental devices used in the MFC for deposit characterization. In this case, pyrometers, probes, laser range finder etc. are in the test section of the MFC.

Sampled, Real-time Diagnostics

Gas analyzers

Gas composition analyses are provided by two separate systems that operate simultaneously. The first is a continuous gas analysis system that provides continuous monitoring of CO, CO₂, NO_x, O₂, SO₂, and total hydrocarbons (THC) with ranges and techniques as summarized in Table 1. Non-dispersive infrared detectors (NDIR) measure CO, CO₂, NO_x, and SO₂ concentrations. A magneto-pneumatic oxygen analyzer provides oxygen concentrations. A flame ionization

Table 1 Summary of on-line gas analysis systems, techniques, and ranges routinely used in the MFC.

<i>Gas</i>	<i>Technique</i>	<i>Range(s)</i>
CO	NDIR	0-200/1000
CO ₂	NDIR	0-5/25 vol %
NO	NDIR	0-300/1500 ppm
SO ₂	NDIR	0-1000/3000 ppm
O ₂	magneto-pneumatic	0-5/25 vol %
THC	flame ionization	0-10/30/100/300/1k/3k/10k/30k ppm

detector is used for THC. The analyzers (Horiba models CFA-321, CFA-311, CMA-321, and FIA-HC) are incorporated in a gas sampling system that controls moisture, temperature, pressure and flowrate of sampled gases. The analyzer repeatability is $\pm 0.5\%$ of full scale when concentrations are greater than 200 ppm and $\pm 1\%$ of full scale for lower concentrations. Zero drift is no more than $\pm 1\%$ of full scale per week for concentrations greater than 200 ppm and $\pm 2\%$ of full scale per week at lower concentrations. Span drift is no greater than $\pm 2\%$ of full scale per week. The exception is the THC measurement, which has a $\pm 1\%$ of full-scale drift per day and a repeatability of $\pm 1\%$. Minimum detectable limits are no more than 0.2% of full scale. Analyzers are typically calibrated before each experiment.

Gas samples are extracted from the combustor through a short ceramic port, pass through an inert, heated fiber filter, and then pass through heat-traced, Teflon-lined sampling line that is maintained above the dew point of the gas. Calibration and span gases are introduced at the probe tip and follow the same flow path as the sample. Sample conditioning for moisture, residual particles, etc. is performed prior to introduction into the analyzer.

Typical interferences from other gases are summarized in Table 2, all of which were measured with nitrogen as the makeup gas.

Table 2 Summary of interferences between various gas measurements in the MFC gas analysis systems.

<i>Gas</i>	<i>Analyzed Concentration</i>	<i>Interfering Gases</i>				
		<i>CO</i>	<i>CO₂</i>	<i>NO_x</i>	<i>O₂</i>	<i>SO₂</i>
CO	192.6			0.00E+00		0.00E+00
CO ₂ dry	143800.0	0.00E+00		-4.17E-06	-3.48E-03	6.95E-06
CO ₂ wet	143800.0			-6.26E-06	-3.48E-03	
NO	961.7	2.08E-04			5.20E-01	0.00E+00
SO ₂	944.0	0.00E+00		0.00E+00		
NH ₃	193.4			0.00E+00		5.17E-03
H ₂ O	9000.0 (5°C)	-4.44E-05	0	0.00E+00	0.00E+00	2.22E-04

The interference data indicate the fractional response of an analyzer to a gas other than the one being analyzed. The strongest interference is NO with O₂, where a 962 ppm concentration of NO is interpreted by the O₂ sensor as 500 ppm O₂. This interference arises because O₂ and NO_x are paramagnetic, with the strength of the NO and NO₂ paramagnetic susceptibility being roughly 43 and 28 % that of oxygen. Oxygen concentrations are accurately determined so long as they exceed those of NO by approximately an order of magnitude. This behavior is typical of all paramagnetic-style oxygen analyzers and is a primary reason such analyzers cannot be used to measure low oxygen concentrations precisely in combustion flows. The remaining interference ratios are two to five orders of magnitude lower and present little concern under typical combustion conditions. Entries that indicate 0.0 indicate no interference was noted. Blank entries indicate no measurements were made.

A second gas analyzer is used simultaneously with the first to prevent temporal drifts in measured NO_x concentrations from biasing the results and interpretation. This analyzer is portable and commonly used on field trips, and is therefore configured with more flexibility, but has less stability than the dedicated system. When not in the field, it is used in the laboratory so we can make simultaneous measurements during experiments. The portable analyzer provides continuous monitoring of CO, CO₂, NO_x, O₂, and SO₂ (no THC, as in the first analyzer) with ranges and techniques as summarized in Table 3.

Table 3 Summary of on-line gas analysis systems, techniques, and ranges routinely used in the MFC.

Gas	Technique	Range(s)
CO	NDIR	0-200/500/1000/2000/5000
CO ₂	NDIR	0-5/10/20 vol %
NO	Chemiluminescence	0-25/50/100/250/500/1000/2500 ppm
SO ₂	NDIR	0-200/500/1000/3000 ppm
O ₂	Galvanic cell	0-5/10/25 vol %

Non-dispersive infrared detectors (NDIR) measure CO, CO₂, and SO₂ concentrations. A galvanic cell oxygen analyzer provides oxygen concentrations. Chemiluminescence is used for NO. The analyzer (Horiba model PG-250) includes particle filtration systems and minimal sample conditioning (moisture control). The analyzer repeatability is $\pm 0.5\%$ of full scale except when CO and NO are below 1000 and 100 ppm, respectively, where repeatability for these gases is $\pm 1\%$ of full scale. Zero drift is no more than $\pm 1\%$ of full scale per day except for the SO₂ analyzer, where zero drift is $\pm 2\%$ of full scale per day. Span drift performs similarly. Linearity is within 2% of full scale. Minimum detectable limits are no more than 0.5% of full scale. Analyzers are typically calibrated before each experiment.

Interferences from other gases are summarized in Table 4, all of which were measured with nitrogen as the makeup gas. The interference data indicate the response of an analyzer to a gas other than the one being analyzed. This instrument is relatively new and we have not measured

the interferences in the laboratory any more precisely than the manufacturer's specifications, which is what is represented in the table.

Table 4 Summary of interferences between various gas measurements in the portable gas analysis systems.

Gas	Interfering Gases						
	H ₂ O 5°C sat.	NO 1000 ppm	C ₃ H ₈ 1000 ppm	SO ₂ 1000 ppm	CO ₂ 20%	CO 5000 ppm	CH ₄ 100 ppm
CO > 200 ppm	±1.0%FS	±1.0%FS	±1.0%FS	±1.0%FS	±1.0%FS		±2.0%FS
CO ≤ 200 ppm	±2.0%FS	±2.0%FS	±2.0%FS	±2.0%FS	±2.0%FS		±2.0%FS
CO ₂	±2.0%FS	±2.0%FS	±2.0%FS	±2.0%FS		±2.0%FS	±2.0%FS
NO	±2.0%FS		±2.0%FS	±2.0%FS	±2.0%FS	±2.0%FS	±2.0%FS
O ₂	±2.0%FS	±2.0%FS	±2.0%FS ¹	±2.0%FS	±2.0%FS	±2.0%FS ³	±2.0%FS
SO ₂	±2.0%FS	±2.0%FS	±2.0%FS ²		±2.0%FS	±2.0%FS	±2.0%FS

¹C₃H₈ at 100 ppm

¹C₃H₈ at 100 ppm

¹CO at 15%

Aerosol Spectrometer

An aerosol spectrometer (Particle Measurement Systems, Inc.) samples and sizes particles in the range of 0.1 - 7.5 µm and is the primary means of characterizing particle size distributions in these experiments. This diagnostic provides complementary analyses to the *in situ* PCSV equipment. The estimated accuracy of the instrument is ± 15% and the demonstrated reproducibility in combustion environments is ± 7%.

Cascade Impactor

Particle size distributions can be both measured and sampled with a Micro-Orifice Uniform Deposit Impactor (MOUDI, Marple et al., 1991) in the size range 0.04 - 5 µm. Smaller size particles can be measured, but not sampled, with the Differential Mobility Analyzer (DMA). Large particles can be sampled and fairly crudely measured using a series of cyclones.

3. Coals and Coal Analyses

The investigations in this report were conducted using a diverse suite of coals (see Appendix 5). The most convenient means of illustrating the range of coals is by name and heating value. Figure 8 illustrates the heating values for 30 of the coals, which includes most of the fuels in the database. The heating values represent moist, mineral-matter free values, which is the basis on which US coals are ranked in the US up to a value of 14000 Btu/lb. Coals with heating values higher than 14000 Btu/lb are ranked based on volatile matter/fixed carbon contents. The coals in the database range in rank from lignites to lv bituminous coals, with the bulk of the coals representing either subbituminous, low-sulfur coals or high-volatile bituminous coals. All coals are of commercial significance.

The analyses in the database are based on as-fired coals in the MFC. Most have been repeated several times as a consequence of many different investigations. However, all analyses are based on pulverized samples. Consequently, most of the fuels are slightly drier and the pyrite in many has slightly oxidized as a consequence of storage and laboratory handling in pulverized form. Therefore, the values represented in Figure 8 are biased to slightly higher values than would be typical of a crushed coal sample in commercial use. This bias is more significant for the low-rank coals than the high rank coals. As-fired heating values in this suite (that is, moist with mineral matter values) range from 4100 to 15000 Btu/lb. Moisture and ash range from less than 1 % to 27% and about 5% to 52%, respectively. However, the bulk of the coals have moisture and ash contents typical of their rank and geographic locations.

Rank, moisture, ash, and heating value represent the most common identifiers for coals in both commerce and science. However, this project is keenly interested in more detailed analyses of the coals and, in particular, of their inorganic components. The remainder of this section discusses our efforts to establish the minimal analyses required to understand inorganic transformations during coal combustion.

Coal Characterization: A Brief Overview

Figure 9 illustrates the relationship of anthracite, coal, lignite, and biomass in terms of the atomic hydrogen-to-carbon (H:C) and oxygen-to-carbon (O:C) ratios. This type of diagram, known as a coalification diagram in the coal science literature, can be used to infer the chemical structure and some combustion and inorganic aspects of coals and other solid fuels. For example, increasing H:C or O:C ratio implies decreasing aromaticity of the fuel. Increasing O:C ratio implies increasing hydroxyl, carboxyl, ether, and ketone functional groups in the fuel. Both the aromaticity and the oxygen-containing functional groups influence the modes of occurrence of inorganic material in fuels and inorganic transformations during combustion.

Inorganic material in solid fuels can be divided into two types: inherent and adventitious. A large fraction of the inherent inorganic material in lignites is associated with oxygen-containing functional groups. These functional groups provide sites for inorganic material to become incorporated in the fuel matrix as, for example, chelates and cations. The potential amount of

Figure 8 Heating values (moist, mineral-matter-free basis) for the coals examined in this work..

Figure 9 Coalification diagram indicating the relationship between a variety of solid fuels in terms of their chemical composition. The labeled regions represent qualitative boundaries for different fuels. The points represent quantitative results of chemical analyses for various materials.

this type of inorganic material is greater in low-rank fuels than in high-rank fuels due, in large measure, to the far higher oxygen content.

The release of this atomically dispersed inorganic material from a fuel particle is influenced both by its inherent volatility and the reactions of the organic portions of the fuel. Material that is inherently volatile at combustion temperatures includes derivatives of some of the alkali and alkaline earth metals, most notably sodium and potassium. Other less volatile material can be released by convective transport during rapid pyrolysis. The amount of fuel lost during the pyrolysis stage of combustion increases with increasing hydrogen to carbon ratio and, to a lesser extent, with increasing oxygen to carbon ratio (see Figure 9). Anthracites typically lose less than 10 percent of their mass by pyrolysis. Bituminous and subbituminous coals lose between 5 and 65 percent of their mass by this process. Lignites, peats, and biomass can lose over 90 percent of their mass in this first stage of combustion. The large quantities of gases or tars leaving coals, lignites, and biomass fuels can convectively carry inorganic material out of the fuel, even if the inorganic material itself is nonvolatile [Baxter and Hardesty 1992; Baxter and Hardesty 1992;

Baxter, Mitchell et al. 1997]. The combination of high oxygen content and high organic volatile matter in subbituminous coals indicates a potential for creating large amounts of inorganic vapors during combustion.

The second class of inorganic material in solid fuels includes material that is added to the fuel from extraneous sources. Geologic processes and mining techniques contribute much of this material to coal. This adventitious material is often particulate in nature (by contrast to the atomically dispersed material) and is the dominant contributor to fly ash particles larger than about 10 μm . Most of the true minerals, as opposed to atomically dispersed inorganic material, are introduced in fuels as adventitious material. Examples include silica, pyrite, calcite, kaolinite, illite, and other silicates.

Fuel analyses can be divided into two broad categories: standard and advanced techniques. Standard techniques include those that have been formally codified by national or international standardization committees. Advanced techniques include approaches that are either in early stages of development or that require equipment that is not commonly available (or both). Procedures for advanced techniques are determined locally rather than nationally or internationally. Standard techniques generally provide information in a format that is well accepted by industrial and scientific communities and of general use, whereas advanced analyses provide more specialized, often less approachable information, typically of most use to specialists.

Standard Analyses

Several standardized methods of fuel analysis are useful in predicting ash deposition tendencies in boilers. Those most uniquely suited to ash deposition analysis include ash chemistry and ash fusion temperature. Other standardized methods useful for ash deposition and other fuel performance analysis include proximate and ultimate analysis, heating value, forms of sulfur, and chlorine. National and international standards describing each of these analyses differ from country to country but generally are more similar than different. The usefulness of these analyses for predicting ash deposition behavior varies. The total ash content (generally determined as part of the proximate analysis) and the composition of the ash (ash chemistry) are essential to any ash analysis. These analyses provide the fuel information that goes into the overwhelming majority of common empirical indices of ash behavior. Ash fusion temperatures are commonly used in contracting and specifying coal behavior, but they commonly fail to predict ash behavior in practical systems. Since these analyses are common, they generally are not discussed in detail here. However, there are a few aspects of the standard analyses that require some detailed comment.

Total Sulfur and Sulfur in Ash

The nominal ash content most commonly reported for coals is that determined during the proximate analysis. This ash typically includes some sulfate. The sulfur content reported in the ultimate analysis is most commonly based on a sample heated to 1350 °C in an oxidizing environment, well above the proximate ashing temperature of, typically, 750-815 °C. There are variations in both the proximate and ultimate temperatures, depending on which standard is being followed. The high temperatures used in the ultimate analysis exceed the thermal decomposition

temperature of all sulfates and carbonates. Indeed, they are specifically chosen for this reason, with sulfates representing by far the more difficult species to decompose. Therefore, all the sulfur in the fuel evolves and is detected during the ultimate analysis. This includes any sulfur that may complex with inorganic materials at temperatures above the proximate analysis but below the ultimate analysis.

Often, 20% or more of the ash from western coals is in the form of sulfates or other forms represented as SO_3 in the ash chemistry analysis. It is important to recognize that this sulfur in the ash is included in the total sulfur analysis of the ultimate analysis. However, it is quite common to see ash (determined from proximate analyses) tabulated with the ultimate analysis. This practice seems almost certain to confuse anyone using the data. If the proximate analysis ash is included with the ultimate analysis, the sum of ash, carbon, hydrogen, nitrogen, sulfur, and oxygen should exceed 100%. The excess arises from a portion of the sulfur is being counted twice, once in the ash and once in the ultimate analysis for sulfur. Since oxygen is normally determined by difference, this confusion potentially biases both the sulfur and oxygen values. Occasionally an investigator notes the discrepancy and renormalizes the data or recalculates the oxygen content. Both adjustments are inappropriate. We generally list ash with the proximate analysis and report ultimate analysis on an ash-free basis to avoid this problem. However, that will not prevent others from including the ash with the ultimate analysis and renormalizing the data.

Sulfur reactions in combustors attract enormous regulatory attention, with total emissions commonly being based for regulatory purposes on fuel sulfur contents. However, that is not our principal concern in this research. A significant fraction of the sulfur in high-rank US coals derives from pyrite, and an accurate estimation of the amount of pyrite in the fuel can be obtained from relatively simple and standardized fuel analyses. However, this estimate will be in significant error if the sulfur content of the fuel is not properly treated.

Finally, this issue has some effect on fuel analysis procedures. When low- and high-rank fuels are ashed together, it is not uncommon that the low-rank ashes contain more sulfur than the total fuel sulfur. This presumably indicates that sulfur emitted from the high-rank coals is fixed in the low-rank ash. In accurate data, the amount of sulfur in the ash should always be less than or equal to the amount of sulfur in the ultimate analysis. Our experience during this project indicates that low-rank fuel analysis violate this rule frequently.

Chlorine

A second issue with standardized analyses is typically of less practical concern and centers around chlorine. Chlorine analyses generally are performed separately from ultimate analyses, if at all. Essentially all of the chlorine in coals is released during the ultimate analysis process. Since oxygen is determined by difference (most typically), failing to account for chlorine as part of the elemental composition of the coal leads to an error in the inferred oxygen concentration in addition to the lack of data on chlorine. Corrections to the oxygen content should be made to account for the presence of chlorine in the evolved gases if oxygen is determined by difference (as is generally the case). However, US coals typically have less than 0.15% chlorine, with 1% chlorine being an extreme upper bound. Oxygen contents, on the other hand, range from 4-20 %,

depending strongly on rank. Typically, chlorine contents are small compared to oxygen contents and the correction to oxygen is often of little practical concern. However, even small amounts of chlorine can have large impacts on inorganic transformations and deposition. Chlorine is much more significant in some international coals and in many fuels fired in conjunction with coal, such as biomass and municipal waste.

Ash

Finally, the term ash is commonly misused or misunderstood. In this document, ash is regarded as a product of coal combustion. Specifically, there is no ash in coal. Ash is formed as the inorganic material in the fuel decomposes, oxidizes, melts, and otherwise reacts during combustion. Similarly, the inorganic portion of fuel is only partly mineral matter. Much of the inorganic material in low-rank coals is atomically dispersed or otherwise associated with the organic fraction of the coal. Such material is not in any mineral form. In this document, we use the term inorganic material to refer broadly to the minerals and other ash-forming components of fuel. Most fuels contain significantly more inorganic material than is suggested by the ash analysis of the fuel. That is, if the proximate analysis indicates 10% ash, there is typically 11-13 % inorganic material in the fuel.

Advanced Analyses

With a few exceptions, standard analyses provide, at most, an estimate of the elemental composition of the fuel. This information is essential to understand the potential behavior of the coal. However, it is clear that further detail is required to improve the accuracy of ash deposition predictions. Compounds with similar elemental compositions behave very differently during combustion, so there is a critical need to develop species-specific information for the inorganic fraction of the fuel. There are a variety of advanced techniques available for determining the species composition of the fuel.

Brief Summary of Principal Advanced Analyses

X-ray diffraction, performed on low-temperature ash, is a powerful tool and the most widely used technique for qualitatively identifying the presence of minerals in their crystalline form in concentrations of a few weight percent or greater. Thermal analytical techniques such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been used as a signature analysis based on changes in physical properties with temperature. Microanalytical techniques, including scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX), electron probe microanalysis equipped with EDX, and transmission electron microscopy (TEM) have very good resolution to very small particle sizes. The techniques may be applied to low-temperature ash as well as raw coal and provide visual images of the morphology of the mineral structure. Extended x-ray analyses (XANE) is another signature analytical technique sometimes applied to coal and petroleum coke. Mossbauer spectroscopy has been widely used for characterizing the mineral forms of iron in coal as well as in slags and deposits.

We have used all of the above analyses to one extent or another in our work, generally in collaboration with other investigators. However, two analyses are selected for more detailed discussion here: Computer-controlled scanning electron microscopy (CCSEM) and chemical fractionation. CCSEM is an increasingly commonly cited technique that measures the chemical

composition and size of individual mineral grains in coal particles. It forms the basis of several models of ash deposition during coal combustion. Chemical fractionation is a non-standardized but relatively accessible technique for characterization of the modes of occurrence of both mineral and non-mineral inorganic material in coal. Some of the most important aspects of these two techniques are reviewed below.

We contend that the combination of standardized analyses and chemical fractionation represents a necessary and sufficient analysis of coals for predicting inorganic behavior. These analyses can be augmented and often improved by other advanced techniques, but the remaining advanced techniques do not provide information necessary for most practical problems. We present the technique for determining species-specific descriptions of all of the inorganic material in coal from these techniques below. While data similar to those that we have generated have been used many times by many investigators, we are not aware that others have previously carried the analysis to the point of complete and species-specific descriptions of the fuel. For this reason, we have completed such analyses on a wide range of coals to compare the trends in the data.

CCSEM

Computer automation of the scanning electron microscope (SEM) coupled with energy dispersive x-ray analysis (EDAX) — commonly referred to as computer-controlled scanning electron microscopy (CCSEM) — is being developed to locate dispersed inorganic particles in coal and quantify their size, shape, and composition. CCSEM analyses are commonly cited as an advanced analytical method of choice. Indeed, CCSEM analyses may be the only known means to determine the joint mineral grain composition and size distributions. When coupled with automated digital image analysis, morphological data can be stored, examined, and used to estimate differences between the included and excluded mineral matter as well as species sharing partially common boundaries of minerals with coal. The technique has been applied to raw coal, partially spent char and fly ash or deposited ash, in effect revealing changes in mineral chemistry at various stages of combustion. We have dedicated considerable effort to the development and analysis of CCSEM procedures. We are perhaps the most circumspect with regard to its current accuracy and utility than are most other laboratories. Here we summarize the instrumental and statistical analyses we have completed for CCSEM characterization of particulate samples.

Figure 10 illustrates the distribution of minerals in a coal sample as determined by CCSEM [Shah, Huffman et al. 1991]. We have completed both independent and collaborative investigations regarding both the qualitative and quantitative accuracy of CCSEM. The qualitative aspects are generally quite useful. However, the quantitative performance of CCSEM is discouraging, as discussed below.

Instrumental and Sample Preparation Issues with CCSEM

Introduction

Scanning electron microscope (SEM) images with electron microprobe analysis (EMPA), combined with energy dispersive x-ray spectrometers (EDS) represent potentially powerful tools for providing morphological and chemical information of materials. Coal researchers have been

Figure 10 Typical CCSEM profile of mineral composition in the small size range.

using this information to characterize joint particle size and composition distributions in raw coals, chars and fly ash [Huffman, Huggins et al. 1989; Loehden, Walsh et al. 1989; Charon, Sarofim et al. 1990; Brekke, Zygarlicke et al. 1991; Shah, Huffman et al. 1991; Galbreath, Zygarlicke et al. 1996; Lee and Lockwood 1999]. Modern technology allows automation computer control of particle recognition, sizing, and chemical analysis steps using SEMs or EMPAs coupled with EDS, making the collection of data for many hundred or a few thousand individual mineral grains possible. This automated analysis technique has been referred to as computer-controlled scanning electron microscopy (CCSEM) analysis [Huggins, Kosmack et al. 1980]. CCSEM analyses provide unique mineralogical and mineral grain size information and is cited as possibly the single most significant developing characterization technique for use in understanding ash transformations during combustion.

CCSEM analysis is based on the SEM/EMPA image generated by the computer; an image we

call the CCSEM image. Any parameters that influence the quality of the CCSEM image also influence the CCSEM results. In the SEM/EMPA, the important parameters affecting CCSEM image quality include: (1) acceleration voltage; (2) threshold level; (3) type of image used; (4) dispersion of mineral grains in the sample; and (5) sample preparation technique. Many of these parameters are chosen by the analyst and differ depending on the material under examination and specific local instrumentation. During our research, we have devoted considerable effort to demonstrate the effect of each of these parameters on the known particle size distributions of well-characterized samples and to recommend means of minimizing uncertainty in results arising from sample-to-sample or analyst-to-analyst variation of these parameters, in particular with regard to their influence on variation in particle size and size distribution results. Implications regarding determination of chemical composition are mentioned, but no detailed analyses or comparisons of chemical composition results are included.

The objectives of our investigation were to: (1) quantify the impact of instrument and sample preparation alternatives on results from CCSEM analyses, and (2) recommend techniques for minimizing the uncertainties in the data introduced by such techniques.

Materials and Equipment

Two types of samples were prepared as surrogate coal mineral grains for this study: a palladium-rhodium alloy and a mixture of tantalum and copper. The Pd-Rh alloy is a convenient material from which spherical particles can be generated in a controlled way. The Ta mixture with spherical Cu particles provides a convenient source of irregularly shaped and physically overlapped metals that can be generated in a controlled manner.

Two sample preparation techniques were used for each material. The first involves dispersing the metal particle in an epoxy resin. This epoxy mixture is then cross sectioned and the surfaces are polished to provide a flat surface for analysis. The second preparation technique involves attaching dispersed metal particles on an aluminum substrate. This technique provides an irregular surface from which the particle's three-dimensional morphology can be determined.

The results that we obtained and analyzed are derived exclusively from SEM data. A JEOL scanning electron microscope model 35 C and a Tracor-Northern energy dispersive x-ray spectrometry (EDS) model TN 5600 are employed in these analyses. The CCSEM software used in the current study is Tracor-Northern's Particle Recognition and Characterization (PRC) program, which is capable of computing size and composition and counting the particle number. While no results from EMPA instrumentation are illustrated below, the general conclusions and recommendations are similar.

Experimental Procedure

A block diagram of the steps performed in CCSEM analysis is illustrated in Figure 11. All particle size information is based on the CCSEM and PRC images, therefore this research focuses on these images and the effect of instrument and sample preparation parameters on their quality and interpretation.

Figure 11 Block diagram for CCSEM analysis of coal-derived samples.

Three types of images are discussed here: the SEM/EMPA image, the CCSEM image, and the PRC image. The SEM/EMPA image is either a secondary electron image (SEI) or backscattered electron image (BEI). In both cases, the image consists of a map of the sample surface, with the brightness of the map at any given location being proportional to the number of electrons being collected by the detector from that location. The quality of the image (spatial and intensity resolution) is instrument dependent.

The CCSEM image is derived from a conventional SEM/EMPA image after it is translated into the computer-controlled particle imaging analyzer. When the electron beam detects a signal exceeding an operator-defined threshold value, the feature is recognized as part of a particle. The CCSEM image is the composite of all pixels in which the detected signal exceeds this threshold value. When the brightness of a feature is below the threshold level, it will be seen in the SEM/EMPA image, but it will not be included in the CCSEM image.

The PRC image is a record of the beam activity during particle detection and size determination. It is used to: (a) identify particles being counted and analyzed; (b) show the location of particle

centroids from which the size and composition are being measured and computed; and (c) compare with the corresponding SEM/EMPA image to determine whether the CCSEM image and its computation is a faithful representation of the actual sampling area.

The algorithm for particle recognition and size determination is schematically illustrated in Figure 12(a) in diagrams that relate directly to the PRC image. A typical PRC image is shown in Figure 12(b) for comparison.

Figure 12 Schematic diagram (a) and PRC image (b) illustrating the steps performed during grain recognition and characterization. The white nodes in the three examples in part (a) indicate bisection points and the solid nodes indicate the center as determined by the particle recognition and characterization software.

The algorithm is as follows:

1. When the electron beam detects a particle, a horizontal chord is constructed between the two opposite particle edges.
2. A vertical cord is constructed that spans the particle and that bisects the horizontal cord obtained in Step 1.
3. A second horizontal chord is constructed that spans the particle and bisects the vertical cord obtained in Step 2.

4. Steps 2 and 3 are repeated until the centers of the vertical and horizontal chords coincide. The centroid is established as this point.
5. A set of chords (up to 16) are drawn through the centroid at equally spaced angles. The particle diameter is determined by the arithmetic average of the lengths of these cords.
6. EDS measurement of particle chemical composition is based on a 1 to 4 μm diagnostic volume centered at the particle centroid.

The size of the diagnostic volume during EDS chemical analysis depends on the material being analyzed, the accelerating voltage, and the angle of incidence of the electron beam. High acceleration voltages ($> 25 \text{ kV}$) and low atomic numbers (< 20) of the material being analyzed lead to large diagnostic volumes, possibly as large as 3 to 4 μm . More typically, diagnostic volumes are confined to 1 to 2 μm .

The waveform of the SEM image contrast and brightness from the sampling area are used as a basis for setting CCSEM imaging threshold. These are shown in many figures, and are indicated with a bright X, throughout this paper.

The test matrix designed for the current study is shown in Table 5 and Table 6. Tests 1 to 5 are designed for demonstrating the threshold level effect and Tests 6 and 7 are for the image type effect. Tests 8 and 9 provide information on the effect of the accelerating voltage. In this case, we determined the size distribution of the particles in the SEM image manually to compare with those determined automatically by CCSEM. This manually collected data serves as the standard against which the data from the automated procedure is compared, allowing us to assess both precision and accuracy of the techniques.

Table 5 Experimental Parameters for the Investigation of the Effects of Instrument Parameters and Sample Preparation on CCSEM Results.

<u>Variables</u>	<u>Level Effects</u>	
	Low	High
Threshold Level*		
Sample Preparation	Cross Sectioned	Particulate (As-Glued)
Sample Geometry	Spherical	Irregular
Image Type	SEI**	BEI***
Accelerating Voltage (KV)	10	25

* Level of brightness above which the particles will be counted.

** Secondary Electron Image

*** Backscattered Electron Image

Table 6 Experimental Design for the Investigation of the Effects of Instrument Parameters and Sample Preparation on CCSEM Results.

Test Number	Sample Morphology	Sample Preparation	Threshold Level	Image Type	Accelerating Volatage (KV)
1	Spherical	As-Glued	69	SEI	20
2	Spherical	As-Glued	82	SEI	20
3	Irregular	As-Glued	62	SEI	20
4	Irregular	As-Glued	96	SEI	20
5	Irregular	As-Glued	114	SEI	20
6	Spherical	As-Glued	69	SEI	20
7	Spherical	As-Glued	69	BEI	20
8	Spherical	Cross Sectioned	69	BEI	10
9	Spherical	Cross Sectioned	69	BEI	25

Results

The effects of threshold level setting, image type, and acceleration voltage on particle size distributions are discussed individually below.

Effect of the Threshold Level Setting.

Figure 13 illustrates: (a) the secondary electron image of a Pd-Rh particle; (b) the PRC image of the same sample; (c) the waveform, with the threshold level arbitrarily set at 69 (arbitrary units); and (d) a histogram of the number of particle vs. particle size as determined by the CCSEM and as determined manually.

As is illustrated, the CCSEM analysis indicates a total of nine particles, as compared with forty particles counted manually. The CCSEM-generated particle size distribution indicates far fewer small particles and far larger average particle size as compared to the standard data. The PRC image (b) indicates that many centroids located by the CCSEM technique are off center. Several are located at or near particle edges where neighboring particles are within a micron of the centroid. Chemical analyses of these particles at the indicated centroids would include a contribution from the neighboring particles, contributing to inaccuracy or imprecision in the overall CCSEM technique.

Figure 13 Illustration of (a) an SEI of Pd spheres, (b) the PRC image of the same sample, with X representing the location used to generate the waveform illustrated with its threshold (set at 69) indicated in (c), and (d) the actual and measured particle size distributions. Compare with Figure 14.

The effect of changing the threshold value is illustrated by Figure 14. These results differ from those in the previous figure only with respect to the threshold level setting, which has been changed from 69 to 82. There is a notable improvement in both the number and size distribution of the detected particles. The number of detected particles changes from nine to twenty-eight. Although this is a large improvement, it is still rather inaccurate when compared to the manually determined number of 40. The agreement between the manually determined and automatically determined particle size distribution is also greatly improved, although the general trend of missing the small particles and including several that are oversize is still evident. There also continue to be many particles whose computed centroids are far removed from the actual center of the particle. Also, this high threshold value produces discontinuities near the centers of some particles, as indicated in Figure 14(b) by discontinuous horizontal lines. These discontinuities cause the affected solid particles to be broken up into two or more sections, leading to an inaccurate size and inaccurately located centroid of the particle.

Figure 14 Illustration of (a) an SEI of Pd spheres, (b) the PRC image of the same sample, with X representing the location used to generate the waveform illustrated with its threshold (set at 82) indicated in (c), and (d) the actual and measured particle size distributions. Compare with Figure 13.

These trends are even more dramatic when particle samples are either irregularly shaped and/or physically overlapped. This is illustrated in Figure 15 for the Cu-Ta samples at three threshold levels. The number of particles detected increases by more than a factor of 2 for these samples. These results indicate that inappropriately determined threshold values can cause the particles analyzed by CCSEM to be a poor representation of the sampling area shown by the SEM image Figure 15 (d) and that it may not be possible to select a threshold that is capable of properly distinguishing particles if they are not well dispersed or if they have irregular shapes.

Effect of Image Type

The effect of using SEI rather than BEI in producing the CCSEM image is illustrated in Figure 15 and Figure 16, which show the secondary electron image, PRC image, BEI image, particle size distribution, and waveform with threshold level of 69, respectively. Both the manually and automatically determined particle size distributions are shown. Arrowheads in Figure 16 indicate how the SEI technique produces brighter particle edges than centers. The remaining portions of the figure are identical to those in Figure 13 (c) and are discussed above.

Figure 15 Illustration of PRC images of the Cu-Ta mixture in cross section with threshold levels at (a) 62, and (b) 96. The backscattered electron image (BEI) of the same sample is indicated in (c), and a comparison of the total number of particle counts in indicated in (d).

Figure 16 Similar to Figure 13(c) with arrows indicating distinctive aspects of wave forms produced around particles when secondary electron images (SEI) are used. Compare with Figure 17(c).

By contrast, Figure 17 illustrates the same sample as viewed by BEI. Arrowheads in Panel c indicate how the BEI technique produces a brighter image at the particle centers than at the edges, in contrast to those in Figure 16. At the same threshold setting, the particle size distribution as determined by BEI indicates a total of 22 particles, with the measured particle size distribution qualitatively similar to the manually determined value. The CCSEM technique is also more successful at finding the particle centers when working with the BEI than when working with the SEI, as illustrated in Figure 17(b). There is a clear improvement in using the BEI, although the results are still only qualitatively accurate.

Figure 17 Illustration of the same sample as is used in Figure 13, Figure 14 and Figure 16, except that it is obtained as a backscattered electron image (BEI). Illustration of (a) the BEI of Pd spheres, (b) the PRC image of the same sample, with X representing the location used to generate the waveform illustrated with its threshold (set at 69) indicated in (c), and (d) the actual and measured particle size distributions. Compare (c) with Figure 16.

Effect of Accelerating Voltage (kV).

Figure 18 illustrates the effect of varying the accelerating voltage (kV) on sample results. Panels a-d of this figure indicate (a) the image of a cross-sectioned sample as indicated by BEI, (b) the waveform with an accelerating voltage of 10 kV, (c) the waveform when using an accelerating

voltage of 25 kV, and (d) the measured particle size distributions for the two accelerating voltages.

Figure 18 Illustration of (a) BEI of cross-sectioned Pd-Rh particles, (b) a waveform with accelerating voltage at 10 kV, (c) a wave form with accelerating voltage at 25 kV, and (d) a comparison of the measured particle size distributions.

There is a significant increase in the contrast at 25 kV as shown by the waveform Figure 18(c). The total numbers of particles counted at 10 and 25 kV accelerating voltage are 35 and 28, respectively. The manually determined number is 97. The particle size distribution determined by CCSEM at 10 kV is smaller as compared to that determined at 25 kV. The actual particle size distribution determined manually contains more small particles than are indicated at either accelerating voltage.

Summary and Discussions

The above results quantitatively indicate several ways that instrumental parameters and sample preparation techniques influence the CCSEM image, the basis of the CCSEM analysis. Increasing accelerating voltage, decreasing threshold level, using SEI as opposed to BEI, and dispersing the sample inadequately all affect the CCSEM results in the same way, namely; (1) the average particle size artificially increases, (2) the number of grains or particles significantly

decreases, (3) particle size distributions skew toward larger sizes, and (4) particle centroids are inaccurately located and, in many cases, are located on particle edges. These effects have to do with a combination of instrumentation, particle overlap, software and sample preparation techniques.

There are implications of these results for routine CCSEM analysis of coal, char, and fly ash samples involving both particle sizing and mineralogy information. The trends in particle sizing are clear. Quantitative size distribution information will require careful attention to dispersing small particles and resolving their sizes. Threshold values for determining mineral grain vs. background or coal particle regions of the image can lead to significant errors at both extremes.

Determination of particle chemistry is compromised when centroids are located off the center of the particle or when particles are physically overlapped. Reasons for off-center centroids are illustrated in Figure 12. Improperly determined centroids are difficult to avoid with coal-derived samples, where mineral matter comprises a large variety of irregularly shaped individual grains.

In summary, quantitative physical and chemical analyses by the CCSEM technique can only be achieved when careful attention to the details of sample preparation and instrument settings are practiced. Samples that deviate from this nature could complicate the resulting interpretation and be significantly misleading.

Recommendations for Sample Preparation and Instrument Issues

Compared with any destructive analytical techniques, such as wet chemical analyses or surface area measurement for sizing, CCSEM analysis requires more on-site judgements in parameter selections from the analyst. This judgement usually is dictated by the individual's knowledge and understanding of electron optics and physics of SEM/EMPA, instrument configuration, and the type of material to be analyzed. For a given sample, it is unlikely and should not be expected that any two different laboratories would produce identical combinations of CCSEM operating parameters.

Based on the above-demonstrated effects of various parameters on the CCSEM analysis, and recognizing the possible sources of variation in selecting operating parameters, significant near-term emphasis should be placed on minimizing the analyst-to-analyst and laboratory-to-laboratory variations. To this end, the following recommendations are made with regard to CCSEM analysis:

- Produce a standard sample(s) as a reference, specifically for the CCSEM analysis. The material used for the standard sample should be chemically and morphologically stable with respect to aging and similar to those materials found in coal
- Establish the correct size distributions and chemical composition of some definable region of this sample. The sample should be routinely circulated among the laboratories performing CCSEM as a quality control (consistency) check. We suggest that the sample be mounted in epoxy, prepared in cross section, and analyzed in BEI mode.

- Round robin tests should be conducted every few years with blind, but well-characterized, samples.
- SEM/EMPA images should routinely be compared with the PRC image of the samples to minimize the uncertainty due to possible local instrument variations.

Statistical Analysis of CCSEM

There are important statistical considerations associated with CCSEM-style analyses that are independent of the instrumental analyses. An appreciation for these can be gained by considering the sample size. A typical CCSEM analysis examines 1,000 to 2,000 mineral grains. If the average size of these grains is 10 μm , and their average specific gravity is 2.5, this represents between one and three micrograms of material (2.6 μg for 2000 particles). Additionally, only a random cross section of these particles is analyzed (to a depth of less than 1 μm), further decreasing the effective mass of material under analysis. It is difficult to sample a sub-microgram quantity of material that is representative of any significant amount of coal, and this fact alone should give one pause before relying on CCSEM analyses for quantitative coal information. However, in this section we exclude consideration of the instrumental issues discussed earlier and the sampling issues just mentioned. Here we presume to have error-free sampling and instrumental techniques and examine the issue sample statistics.

Probability Density Functions

It is useful to have some model of particle size distributions in mind when analyzing data. One commonly cited distribution for particle sizes is the log-normal distribution. If a random variable x is normally distributed, and a second random variable y is related to x as

$$y = e^x, \quad (1)$$

then the variable y has a log-normal distribution. The log-normal distribution is given by

$$f(d; \mu, \sigma) = \frac{\exp\left[-\frac{(\log(d) - \mu)^2}{2\sigma^2}\right]}{\sigma d \sqrt{2\pi}} \quad \text{for } x \geq 0 \quad (2)$$

$$0 \quad \text{otherwise}$$

where d represents diameter and μ and σ represent the mean and standard deviation of the underlying normal distribution (the distribution of x , not y , in the terms of Eq. (1)). The expected value (mean) and variance (square of the standard deviation) of the log normal distribution are given by

$$E(D) = \exp\left(\mu + \frac{\sigma^2}{2}\right) \quad (3)$$

and

$$V(D) = \exp(2\mu)[\exp(2\sigma^2) - \exp(\sigma^2)] \quad (4)$$

respectively. It is important to note that μ and σ have no simple relationship to the expected value and the standard deviation of the log-normal distribution, as indicated by these equations. This distribution is generally used to describe the number distribution of particles. Figure 19 and Figure 20 illustrate the log-normal distribution and its dependence on its parameters, together with its calculated expected values and variances.

The mean value of the mass is related to the expected value of the cube of the diameter. In general, the expected values of the diameter raised to any power is given by the moment generating function

$$E(D^n) = \exp\left(n\mu + \frac{n^2\sigma^2}{2}\right) \quad (5)$$

and, in the case of the cube of diameter, this yields

$$E(D^3) = \exp\left(3\mu + \frac{9\sigma^2}{2}\right) \quad (6)$$

One of several qualitative features of the log-normal distribution is that the probability of a negative value of the independent variable is zero. This is consistent with its use for size distributions and other non-negative data. However, this feature leads to some confusion for people accustomed to working with normal distributions. For example, in a normal distribution, about 68% of the sample lies within one standard deviation of the mean, with about 32% lying outside this range. If there are to be no negative values in a normal distribution, the mean must be many times larger than the standard deviation. In the case of a log-normal distribution, the standard deviation commonly exceeds the mean, even though there are no negative values. Such is the case for both examples in Figure 19 and Figure 20.

Figure 19 Log-normal distributions with specified parameters, expected values, and standard deviations.

Figure 20 Same data as in Figure 19 plotted on a logarithmic scale, revealing the underlying shape of a normal distribution.

Statistics of the Mean

We now want to examine the statistics of determining quantities such as size distributions and average composition by sampling particles from such a distribution. We assume that

$$T = \frac{(\bar{x} - \mu)\sqrt{n}}{s} \quad (7)$$

follows a Student's t distribution with $n - 1$ degrees of freedom and describes the statistics of, for example, the mass-average of the particle size distribution. Here, $\bar{x}$ represents the measured mass-average particle size of the inorganic particles, μ is the true mass-average particle size of the sample (which is not related to the previously discussed parameter of the log-normal distribution), s is the measured standard deviation, and n is the number of samples used to determine $\bar{x}$ and s . Eq. (7) is valid for any quantity sampled from a normal distribution. According to the Central Limit Theorem, it is also valid for quantities determined from other distributions so long as they don't maximize near their limits and so long as a large number of samples are evaluated. Log-normally distributed particle sizes (and most any other distribution of particle sizes) fit appropriately within these bounds. We want to determine the number of particles that must be sampled to determine $\bar{x}$ within $p\%$ of μ with $\alpha\%$ probability. For example, if p is 10% and α is 95%, we will determine the number of samples required to be 95% certain that the measured mass average diameter of these samples is within 10% of the true mass-average diameter. The required sample size is determined from

$$n = \left(\frac{T_{n-1}^{-1}(\alpha)s}{\mu p} \right)^2 \quad (8)$$

where $T_{n-1}^{-1}(x)$ represents the inverse Student's t distribution with $n - 1$ degrees of freedom, that is, the value of the random variable T that includes $x\%$ of the total area within $\pm T$. When sample sizes grow large, the Student's t distribution becomes indistinguishable from a Gaussian or normal distribution. As an example, if we assume that the experimentally determined mean of the ash particles is approximately half the standard deviation, and that we want to be 95% certain that we have determined the total inorganic content within ten percent of its true value, the total number of particles that must be sampled is about 1537. (Values of the Student's t and normal or Gaussian distributions are available in most statistics texts [Canavos 1984]. At 95% certainty with samples this large, the distributions yield values of $T_{n-1}^{-1}(x)$ of 1.96).

Assuming that an individual inorganic species represents $q\%$ of the total inorganic mass. The fraction of all particles that are composed of this species is then given by

$$\frac{n_{species}}{n_{total}} = q \frac{\langle \rho \rangle_{total}}{\langle \rho \rangle_{species}} \left(\frac{\langle d \rangle_{total}}{\langle d \rangle_{species}} \right)^3 \quad (9)$$

where all quantities in angle brackets represent mass averaged values, ρ is density and d is diameter. As a specific example with some typical values, assuming we are interested in pyrite, that specific gravity of the average inorganic grain is about 2.5, the specific gravity of pyrite is 5 and that the average pyrite grain is approximately twice the size of the overall average. If we further assume that pyrite comprises 10% of the total inorganic mass, the ratio of pyrite grains to total grains is about 1 in 160. If we want to determine pyrite to within ten percent of its true value with 95% confidence, we must therefore sample about $160 \times 1537 = 245,920$ particles. Even with automated procedures, this is unfeasible. Typical CCSEM analysis include approximately 1000-2000 particles, less than 1% of the required number to obtain even $\pm 10\%$ accuracy in the typical example of pyrite cited here. At this sampling rate, we can not expect to determine even the average pyrite (or inorganic material) concentration with any reasonable degree of accuracy. Round-robin examinations of the technique reflect such inaccuracies.[Galbreath, Zygarlicke et al. 1996].

The number of required particle analyses depends on the fraction of the total material comprising a species, the desired accuracy and confidence in this accuracy, the size and density of the particles relative to that of the average inorganic material, and the mean and variance of the overall particle size distribution. These dependencies are quantitatively indicated above. However, under essentially all cases of practical interest, a reasonable estimation of the average composition of the inorganic material requires a significantly larger number of particle analyses than is practical with current technologies.

Statistics of Higher Order Moments and Modes of Occurrence

However, CCSEM analyses divide the data much finer than is required to obtain average composition information. Typically, the size distribution of an inorganic species is estimated as the number of particles in approximately five size bins on a species-by-species basis, commonly resolved into about ten species. As the number of size bins and the number of inorganic species increases, the sampling statistics indicated here become increasingly worse. This is one cause of the discouraging results from precision trials with CCSEM analyses.

Finally, there are serious steric issues in interpreting CCSEM data. As an example, CCSEM data are sometimes used to distinguish extraneous inorganic material from inherent material. A coal boundary next to the inorganic grain distinguishes an inherent or included inorganic grain from an extraneous inorganic particle. Trying to distinguish among coal, epoxy, and inorganic grains greatly compounds the instrumental issues discussed earlier. However, a more fundamental problem is that there are many ways that random cross sections of particles can intersect included inorganic grains such that there are no coal boundaries in the plane. However, there is no means by which excluded particles can be cross sectioned to produce a coal boundary next the particle (unless the particles are poorly dispersed). The resulting inaccuracies and bias in estimating the

amount and composition of excluded inorganic grains lead to unrealistically high estimates of excluded inorganic material, as is evidenced in the reports using such techniques.

Finally, the statistics of quantities such as the variance and higher orders of the pdf require much larger sample sizes for comparable confidence. As has been indicated, CCSEM poorly estimates the average composition and size of most species under the conditions most commonly used for the analysis. The estimations of the size distribution are much poorer still.

Overall Conclusions Regarding CCSEM Analyses

Presently, these techniques, although commercially available, require the skills of a highly trained scientist and are expensive. The services for determining analysis via these techniques are provided by only a few laboratories, limiting their availability. Widespread practical application requires more extensive demonstration of their utility in predicting and solving problems and an increase in precision and accuracy.

Chemical Fractionation

One technique that offers significant, species-specific information and can be performed by any laboratory capable of performing common standardized analyses is chemical fractionation. Chemical fractionation was originally developed by Miller and Given and uses selective extraction of elements, based on solubility, which reflects their association in the fuel [Miller and Given 1978]. We have performed a reasonably extensive investigation of the qualitative accuracy and quantitative precision of chemical fractionation. The specific procedure we use is summarized in Appendix A1. The process consists of three successive extractions. The first is by water and is intended to remove water-soluble elements such as sodium. The second extraction uses ammonium acetate to remove elements such as sodium, calcium, and magnesium that are ion exchangeable. The third extraction uses hydrochloric acid to remove acid-soluble species such as alkaline earth sulfates, carbonates, etc. The residual material typically consists of silicates, oxides, and sulfides.

This wet-chemistry technique is not ideal in that it can easily be biased by incomplete penetration of the fuel by the solutions, partially soluble compounds, and other vagaries. However, when carefully performed, we find that it is both accurate and precise, nearly within the limits of the elemental analysis procedures themselves [Baxter and Hardesty 1992; Baxter and Hardesty 1992].

Table 7 and Table 8 summarize some of the inorganic species and mineral groups found in coal or in its high-temperature products. The chemical composition of many minerals varies, and there are some disagreements among mineralogists and even more disagreement within the coal community as to which mineral names are associated with which specific compositions. This table uses standard compositions and indicates the variations where they exist.

Table 7 Major compounds in each of the classes indicated in Figure 23.

Class	Prominent member for most coals	Typical fraction of total inorganic material	
		Low Rank	High Rank
Sulfides	Pyrite	3%	16%
Halides	Chlorides	1%	0.5%
Oxides and Hydroxides		55%	32%
Oxides	Silica, Rutile	24%	24%
Hydroxides	atomically dispersed material, inter-clay material	31%	8%
Carbonates	Calcite	12%	1%
Sulfates	Gypsum, Mirabilite	1%	6%
Phosphates	Calcium phosphates	1%	0.5%
Silicates		26%	44%
High Melting	Kaolinite, Mullite	22%	28%
Low Melting	Illite, Biotite	4%	16%
Mineraloids	Opal	1%	3%

Many of the species indicated in Table 7 and Table 8 can be distinguished by chemical fractionation. The key to doing so is to compare the elemental composition of the materials extracted at each stage of the process. Table 9 represents the key to such a comparison as a function of solubility and species name. In general, the coefficients indicated in the table for each of the elements can be used as a matrix to determine the species composition of the material. That is, if matrix A represents the coefficients for one of the solubility classes (water, ion exchangeable, acid, or residual) indicated in Table 9 and is row-ordered according to species and column ordered according to element, and matrix X is a column matrix representing the unknown amounts of the chemical species, in the same order as the rows of matrix A, then

$$Ax = B \quad (10)$$

where B a column matrix of elements in the same order as the columns of A that represents the amount of each element removed within the solubility class. The amounts of the species are found by inverting A and multiplying both sides in a traditional way, i.e.,

$$x = A^{-1}B \quad (11)$$

Adding the constraint that the matrix X must be positive definite, completes a first-order analysis of species composition.

In practice, there are some complications. First, not all of the elements can be reliably determined from chemical fractionation. Specifically, it is not always possible to distinguish sulfur from the organic coal matrix from inorganic sulfur during fractionation. Also, chlorine can not be determined for either the acid soluble or residual step because of the chloride in the

Table 8 Mineral groups, names, formulas, and characteristics of commonly occurring minerals in coal.

Group	Mineral/Inorganic Material	Formula	Notes
Clay	Montmorillonite	$(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n(\text{H}_2\text{O})$	
	Illite	$\text{KAl}_2\text{Si}_3\text{AlO}_{10} \bullet \text{H}_2\text{O}$	Aluminum-rich end member of illite (closely related to mica mineral muscovite)
		$\text{KMg}_2\text{Si}_3\text{AlO}_{10} \bullet \text{H}_2\text{O}$	Magnesium- and aluminum-rich end member
		$\text{KFe}_2\text{Si}_3\text{AlO}_{10} \bullet \text{H}_2\text{O}$	Iron- and aluminum-rich end member
		$\text{KAl}_2\text{Si}_4\text{O}_{10} \bullet \text{H}_2\text{O}$	Aluminum- and silicon-rich end member
		$\text{KMg}_2\text{Si}_4\text{O}_{10} \bullet \text{H}_2\text{O}$	Magnesium- and silicon-rich end member
		$\text{KFe}_2\text{Si}_4\text{O}_{10} \bullet \text{H}_2\text{O}$	Iron- and silicon-rich end member
	Kaolinite/ Halloysite	$\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2 \bullet 2\text{H}_2\text{O}$	
	Muscovite	$\text{KAl}_2\text{Si}_3\text{AlO}_{10} \bullet \text{H}_2\text{O}$	
Feldspars	Orthoclase/ Microcline	KAlSi_3O_8 (Or)	Potassium-rich feldspar end member.
	Sanidine	Or ₅₀₋₈₀	High-temperature alkali feldspar intermediate between Or and Ab
	Anorthoclase	Or ₂₅₋₆₀	High-temperature alkali feldspar intermediate between Or and Ab
	Perthites	Or _x Ab _y	Low-temperature alkali feldspar intermediate between Or and Ab
	Albite	$\text{NaAlSi}_3\text{O}_8$ (Ab)	Sodium-rich plagioclase/feldspar end member
	Oligoclase	Ab ₇₀₋₉₀	Intermediate plagioclase between Ab and An (exists at all temperatures)
	Andesine	Ab ₅₀₋₇₀	Intermediate plagioclase between Ab and An (exists at all temperatures)
	Labradorite	Ab ₃₀₋₅₀	Intermediate plagioclase between Ab and An (exists at all temperatures)
	Bytownite	Ab ₁₀₋₃₀	Intermediate plagioclase between Ab and An (exists at all temperatures)
	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$ (An)	Calcium-rich plagioclase end member
Silicates	Biotite	$\text{K}(\text{Mg,Fe}^{++})_3(\text{Al,Fe}^{++})\text{Si}_3\text{O}_{10}(\text{OH})_2$	Phyllosilicates (layered) Mica like layered silicates with $[\text{Si}_4\text{O}_{10}]_4$
	Mullite	$3\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2$	
	Gehlenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$	
	Meta-kaolinite	$\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2$	
	Liebenbergite	Mg_2SiO_4	Olivine group
	Fayalite	Fe_2SiO_4	Olivine group
Oxides	Quartz/ Tridymite/ Cristobalite	SiO_2	Quartz is dominant low-temperature phase
	Rutile	TiO_2	
	Magnetite	Fe_3O_4	

Carbonates	Hematite	Fe_2O_3	
	Spinel	MgAl_2O_4	
	Calcite/ Ankerite	CaCO_3	
	Magnesite	MgCO_3	
	Siderite	FeCO_3	(Common in Australian coal. Rare in US coal.)
Sulfates	Dolomite	$\text{CaMg}(\text{CO}_3)_2$	
	Gypsum	$\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$	
	Ferrous Sulfate	FeSO_4	
	Melanterite	$\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$	
	Mirabilite	$\text{Na}_2\text{SO}_4 \bullet 10\text{H}_2\text{O}$	
	Arcanite	K_2SO_4	
	Kalinite	$\text{KAl}(\text{SO}_4)_2 \bullet 12\text{H}_2\text{O}$	
	Ferrous Sulfate	FeSO_4	
	Ferric Sulfate	$\text{Fe}_2(\text{SO}_4)_3$	
	Glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$	
	Epsomite/ Epsom Salts	$\text{MgSO}_4 \bullet 7\text{H}_2\text{O}$	
	Alunite	$\text{KAl}_3(\text{SO}_4)_2 \bullet 12\text{OH}$	Widespread in western US
	Alunogen	$\text{Al}_2(\text{SO}_4)_3 \bullet 17\text{H}_2\text{O}$	Occurs near pyrite
Sulfides	Pyrite / Marcasite	FeS_2	
	Pyrrhotite	Fe_7S_8	
Phosphates	Hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3 \bullet \text{OH}$	
	Calcium Phosphate	$3\text{CaO} \bullet \text{P}_2\text{O}_5$	
	Calcium	$2\text{CaO} \bullet \text{P}_2\text{O}_5$	
	Pyrophosphate		
Halides/ Hydroxides	Halite	NaCl	
	Sylvite	KCl	
	Sodium Hydroxide	NaOH	
	Potassium Hydroxide	KOH	
	Calcium Hydroxide	$\text{Ca}(\text{OH})_2$	
	Magnesium Hydroxide	$\text{Mg}(\text{OH})_2$	

Table 9 Elemental ratios and solubilities of major inorganic species found in coal.

	Formula	Si	Al	Ti	Fe	Ca	Mg	Na	K	P	S	Cl
Residual	Montmorillonite											
	NaAl ₆ Si ₁₂ O ₃₀ (OH) ₆ •nH ₂ O	12	6					1				
	CaAl ₆ Si ₁₂ O ₃₀ (OH) ₆ •nH ₂ O	12	6			1						
	NaAl ₃ Mg ₃ Si ₁₂ O ₃₀ (OH) ₆ •nH ₂ O	12	3				3	1				
	H ₂ O											
	CaAl ₃ Mg ₃ Si ₁₂ O ₃₀ (OH) ₆ •nH ₂ O	12	3			1	3					
	Illite											
	KAl ₂ Si ₃ AlO ₁₀ •H ₂ O	3	3						1			
	KMg ₂ Si ₃ AlO ₁₀ •H ₂ O	3	1				2		1			
	KFe ₂ Si ₃ AlO ₁₀ •H ₂ O	3	1		2				1			
	KAl ₂ Si ₄ O ₁₀ •H ₂ O	4	2						1			
	KMg ₂ Si ₄ O ₁₀ •H ₂ O	4					2		1			
	KFe ₂ Si ₄ O ₁₀ •H ₂ O	4			2				1			
	Kaolinite											
	Al ₂ O ₃ •2SiO ₂ •2H ₂ O	2	2									
	Orthoclase											
	KAlSi ₃ O ₈	3	1						1			
	Albite							1				
	NaAlSi ₃ O ₈	3	1									
	Anorthite					1						
	CaAl ₂ Si ₂ O ₈	2	2									
	Mullite											
	3Al ₂ O ₃ •2SiO ₂	2	3									
	Quartz											
	SiO ₂	1										
	Rutile			1								
	TiO ₂											
	Muscovite											
	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	3	3						1			
	Hydroxylapatite					5				3		
	Ca ₅ (PO ₄) ₃ •OH					3				2		
	Calcium Phosphate					2				2		
	3CaO•P ₂ O ₅											
	Calcium											
	2CaO•P ₂ O ₅											
	Pyrophosphate											
Water Soluble	Pyrite				1						2	
	FeS ₂											
	Melanterite				1						1	
	FeSO ₄ •7H ₂ O											
	Gypsum					1					1	
	CaSO ₄ •2H ₂ O											
	Glauberite					1		2			2	
	Na ₂ Ca(SO ₄) ₂						1				1	
	Epsomite											
	MgSO ₄ •7H ₂ O							2			1	
Acid Soluble	Mirabilite/ Thenardite											
	Na ₂ SO ₄ •10H ₂ O											
	Arcanite								2		1	
	K ₂ SO ₄											
	Gibbsite		1									
	Al(OH) ₃											
	Hematite				2							
	Fe ₂ O ₃					1						
	Calcite						1					
	CaCO ₃											
Acid Soluble	Magnesite						1					
	MgCO ₃											
	Siderite				1							
	FeCO ₃					1	1					
Acid Soluble	Dolomite											
	CaMg(CO ₃) ₂											

hydrochloric acid. These constraints are not too significant. Chlorine is a minor issue in most US coals and is, in any case, almost entirely water soluble or ion exchangeable in the fuel. The ambiguity with sulfur is also a fairly minor issue. Most of the standardized methods for determining forms of sulfur are based on similar wet chemistry such that the sum of the sulfur removed in the three leachings should correspond to the sulfatic sulfur. If the leached sulfur

significantly exceeds sulfatic sulfur, the sample has probably suffered some weathering/oxidation since the original analysis of forms of sulfur.

There are several, more severe, complications. A detailed examination of Table 9 reveals that the matrix A above will be singular in several cases. This arises when two or more species or combinations of species have the same ratios of elemental composition within one solubility class. In other cases, there may be an insufficient number of species to account for all of the elements. Both of these complications can be addressed by carefully selecting a subgroup of the species listed in Table 9 to use as the basis of the analysis or by determining by other means the ratios between the amounts of species with similar elemental compositions.

This leads to the most significant complication assigning species based on chemical fractionation data — the selection of an appropriate basis set of species and the order in which these species are added to the estimated inorganic composition of the coal. Given the amount of 11 elements extracted in each of three steps plus the residuals, a maximum of $11 \times 4 = 44$ inorganic species concentrations can be estimated. Several authors have documented the existence of far more inorganic compounds in coal. Most of these are in very low concentration and are of interest to trace metal behavior, coal science or other academic pursuits, but are of little practical consequence for ash deposition. An adequate description of the inorganic species in coal for the purposes of ash deposition requires fewer than 44 candidates. For the purposes of modeling, we also need to account for all of the elements in the ash. Even the best fuel characterization data often indicate small quantities of leached material in solubility classes where it is difficult to establish a relevant species. These usually arise from small measurement errors. For example, experimental variation in fuel characterization commonly indicates that a small amount of aluminum or silicon is water soluble. While this is easily ignored in terms of fuel characterization, the mass that it represents must be included in models to allow them to properly converge. Therefore, there are several species in these lists that are rarely found in coal, but which serve the purpose of ameliorating such small errors and preventing modeling problems.

We estimate the species composition of the fuel by inserting species in the matrix A in order of decreasing complexity (in terms of composition) up to (but not including) the point that the matrix becomes singular. We then solve the constrained linear algebra problem briefly outlined above. This typically leaves some residual material not accounted for among the species selected. We repeat the process, continually decreasing the complexity of the species, until all of the mass is assigned to some inorganic species. Using the residual solubility group as an example, the computations proceed conceptually by determining the amounts of rutile, pyrite (from pyritic sulfur) and calcium-based phosphates (from phosphorous), and removing the corresponding amount of titanium (all of it), iron, sulfur, phosphorous (all of the phosphorous) and calcium from the residual solubility pool. Next, we determine the maximum amount of illite that can be formed without forcing any of the remaining amounts of Si, Al, K, Fe, or Mg to be negative. This determines both the amount and the overall composition of illite. Typically, significant Si and Al and smaller amounts of one or two of the remaining three cations are left. The maximum amount of albite, anorthite, and orthoclase that can be formed from the remaining Si, Al, Na, Ca, and K is calculated. From these, the amount and composition of plagioclase and the amount of orthoclase are determined. Typically there remains mainly Al and Si, often with

smaller amounts of some other cations. The maximum kaolinite that can be formed from the remaining Si and Al is then computed, which typically represents the single most concentrated fraction of the inorganic material. Similar, the olivine concentrations are determined. Typically there remains some Si after all other elements have been allocated to other species. This remainder we assume to be free silica. For nearly all coals, this leads to a mineralogy of the residual fraction that includes essentially all phosphorus as calcium phosphate, all titanium as rutile, varying amounts of iron as pyrite, most of the remaining iron as illite, large amounts of kaolinite, varying but significant amounts of free silica, and relatively minor amounts of anorthite, albite, orthoclase, olivines, etc. This is a conceptually accurate description of the composition of residual material in US coals. Similar analyses are completed for the water soluble, ion exchangeable, and acid soluble groups.

Chemical fractionation analyses and interpretation along these lines have been completed for a suite of over 25 coals, nearly all from the US, and ranging in rank from lignites to mv bituminous coals. Representative results from these results that are particularly important to ash deposition are illustrated here.

The sum of the water soluble and acid soluble alkali metals defines the fraction of such material that is mobile, that is, is not tied up in clays or other relatively inert forms. This material is generally atomically dispersed. The fraction of the total alkali metal that is atomically dispersed is a consistent function of rank, as indicated in Figure 21 and Figure 22.

Figure 21 Results from chemical fractionation analyses of sodium as a function of coal rank for a suite of mostly US coals, with rank increasing from left to right.

Furthermore, the trends are in qualitative agreement with well-established coal behaviors. For example, sodium is well established as a potentially serious fouling precursor in low-rank coals but less so in high-rank coals, consistent with its mode of occurrence as determined by chemical

fractionation (see Figure 21). High-rank coals generally contain less sodium than low-rank coals and the sodium that is present in high-rank coals is less mobile than that in low-rank coals.

Potassium is sometimes also implicated as a fouling precursor in low-rank fuels (though less so than sodium) but virtually never in high-rank fuels, even though potassium is slightly more volatile and the potassium concentration in high-rank coals is commonly higher than in low-rank coals. This too is consistent with the modes of occurrence of potassium (see Figure 22 and compare with Figure 21). Essentially all of the potassium in high-rank coals occurs in a mode (typically in illite or other silicates) that inhibits its vaporization and recombination with other elements, making it less of a fouling problem than sodium despite its higher volatility and sometimes higher elemental concentration.

Figure 22 Results from chemical fractionation analyses of potassium as a function of coal rank for a suite of mostly US coals, with rank increasing from left to right.

The results of chemical fractionation analyses can be used to estimate the species composition of both minerals and non-mineral inorganic components in coal. Figure 23 illustrates the fraction of twenty of the most common inorganic species in coal as a function of coal rank. The figure illustrates how silicates, silica, pyrite, and atomically dispersed materials such as hydroxides dominate the total inorganic mass of the fuel. However, the influence of a species on ash transformations and deposition is not always proportional to its mass. Even small quantities of halides, compounds containing mobile alkali, etc. can have large impacts on overall ash deposition behavior.

Minerals are classically grouped into about ten classes: elements, sulfides, halides, oxides, carbonates, sulfates, phosphates, silicates, "organic" minerals, and mineraloids. The last two are

technically not minerals. The "organic" minerals (amber is an example) have crystalline structures, but are of organic origin. The mineraloids (opal is an example) often resemble minerals superficially, but lack crystalline structures. Coal inorganic material includes representatives from each of these classes. However, the amount and importance of inorganic material in the elements and organic minerals classes is very small and will not be further discussed. The inorganic material in our suite of fuels divides into the remaining classes as indicated in Figure 24. Some of the prominent members of each class are displayed separately. The most prominent members of each class are also indicated in Table 7.

Figure 23 Major forms of inorganic material in a suite of US coals, arranged in rank order and by mineral class. See Table 7. Species are presented in the graph from bottom to top in the order indicated in the legend.

Traditional divisions of minerals into classes are not necessarily the most useful analytical approach for our purposes. In particular, hydroxides and oxides behave very differently in combustion environments. Also, a distinction should be made between high- and low-melting silicates. These distinctions are included in the table.

The data as presented thus far are useful to get a general feeling for the inorganic materials found in coal. Quantitative treatment of these data requires the species themselves to be identified. The number of species in coal is too large to conveniently illustrate, but a feeling for the distribution can be obtained from Figure 25. Here, most of the species that can be distinguished by these techniques are indicated. There are a large number of small contributors beyond the half-dozen major forms of inorganic material in any one coal.

Figure 24 Major forms of inorganic material in coal as a function of coal rank as determined by chemical fractionation. Species are presented in the graph from bottom to top in the order indicated in the legend.

Figure 25 Modes of occurrence of inorganic material as a function of coal rank for US coals. Species are presented in the graph from top to bottom in the order indicated in the legend.

4. Transformations

Fly Ash Formation: A Brief Overview

Fly ash formation models are in various states of development by several researchers. Investigators at the MIT Energy Laboratory [Loehden, Walsh et al. 1989] describe a model for the generation of fly ash capable of predicting the size and composition distributions of fly ash from detailed descriptions of coal mineral matter. Similar models based on individual particle viscosity or other parameters are under development by other investigators [Srinivasachar and Boni 1989; Boni, Beér et al. 1990; Boni, Johnson et al. 1990; Srinivasachar, Helble et al. 1990; Srinivasachar, Helble et al. 1990; Srinivasachar, Helble et al. 1990; Srinivasachar, Helble et al. 1990; Srinivasachar, Helble et al. 1991; Srinivasachar, Senior et al. 1992; Zygarlicke, McCollor et al. 1992; Zygarlicke, Ramanathan et al. 1992; Benson, Hurley et al. 1993] building on published fundamental results [Friedlander and Johnstone 1957; Israel and Rosner 1983; Loehden, Walsh et al. 1989; Rosner 1989; Rosner and Tassopoulos 1989]. The output of these models is a description of the size and elemental composition distributions of the entrained particulate phase resulting from the combustion of pulverized coal.

Figure 26 schematically summarizes the fate of the inorganic material in coal in terms of producing a fly ash. A coal particle is illustrated on the left in the form in which it is fired into a combustor. In general, there may be mineral grains imbedded in the particle, as illustrated, or extraneous to the particle itself. The fate of this second class of inorganic material differs substantially from that of the inherent material. The minerals undergo chemical reactions and phase changes determined by their thermochemistry as well as interacting with other inorganic components and the organic material. Components of the minerals may be released from the fuel by either thermal decomposition or vaporization during combustion.

The transformations are divided into two types: release mechanisms and the fate of the residual ash. Release mechanisms are indicated as vaporization, thermal or chemical disintegration of the inorganic material (inorganic reaction), or convection during rapid devolatilization or other organic reactions. These mechanisms tend to produce small ($< 0.1 \mu\text{m}$) particulate or vapors. The residual ash may undergo fragmentation either as a mineral grain or in conjunction with fragmentation of burning char particle, may coalesce with some or all of the remaining inorganic material, and it may undergo significant chemical or physical transformations. This material tends to produce larger ash particles. Depending on the type of inorganic material and the combustion conditions, the ash produced during combustion is composed of varying amounts of vapor, fume ($< 1 \mu\text{m}$ diameter), and larger particulate.

The underlying theme of this discussion is that the behavior of the inorganic matter and the properties of the deposits that are formed from it can be described in terms of a small number of mechanisms. The discussion below outlines this mechanistic approach to describing the fate of inorganic material in coals with a particular focus on the mechanisms of ash deposition. This mechanistic approach has the potential of embracing a large range of variations in coal type (as well as other solid fuels, such as biomass) combustor types, and operating conditions without the

need of developing extensive databases or testing procedures for each new situation. The approach has been successfully demonstrated for coal combustion, and examples from coal experiments will be used as illustrations.

Figure 26 Schematic illustration of the fate of inorganic material in coals during combustion. Inorganic material in the raw coal may be atomically dispersed or in grains. The grains may be imbedded in the coal (as illustrated) or extraneous to it.

Transformations of Representative Species

Most inorganic species do not combust in the same way as coal – pyrite being a notable exception. However, the inorganic species do undergo transformations, forming inorganic gases, vapors, molten particles and solids. These transformations determine the physical and chemical nature of the material depositing on heat transfer surfaces. This discussion starts with the transformations of pure materials, followed by an analysis of how materials interact with several different species are found within the same particle.

Many inorganic materials occur as hydrates in coal, all of which dehydrate upon heating. These species generally dehydrate between 100 and 200 °C (with some dehydrating at higher temperatures) in an endothermic reaction that often consumes more energy than that required to vaporize the water alone.

After dehydration, inorganic transformations are generally similar within the classes of inorganic species indicated in Figure 24. For example, sulfates all thermally decompose as they are heated, as do carbonates and sulfides. In some cases (generally the alkaline earth salts), these salts decompose prior to melting and appreciable vaporization, while in other cases (generally the alkalis) they melt, vaporize and finally decompose in the gas phase. The products of decomposition are the oxides and light, non-condensing gases (CO_2 , SO_2 , etc.).

Chlorides and hydroxides are more stable than the salts with bivalent anions and generally melt and vaporize. At flame temperatures, these species represent the most stable form of the alkali metals and of chlorine and hydroxyl.

Phosphates and silicates undergo transformations when heated but generally do not completely decompose or vaporize. Their melting behavior depends on their composition and structure, and they can generally be grouped into high-melting and low-melting categories. The high-melting species characteristically contain no alkali or alkaline earth metals.

The oxides of all elements except alkalis are quite stable and often are the thermodynamically preferred forms at high temperatures under oxidizing conditions.

The mathematical expressions presented later in this report can be used to predict the decomposition and reaction rates of the inorganic species in coal. A few examples are indicated here from typical combustion systems. In these examples, composition is shown as a function of temperature during the heating period of the particle. In practice, composition is a function of time and not a unique function of temperature. However, under practical conditions many of the transformations occur over such a short time span, due to the very rapid particle heating, that they are difficult to illustrate as a function of time. Therefore, we use representative examples here to illustrate the behaviors as a function of temperature.

Figure 27 illustrates the thermal decomposition of gypsum (hydrated calcium sulfate) during rapid particle heating. As is seen, gypsum dehydrates to form anhydrite (calcium sulfate), which does not decompose until about 1400°C . The transition from anhydrite to calcium oxide occurs at about the same temperature as the melting point of anhydrite. There is essentially no gas-phase species formed at these temperatures from calcium. The amount of both calcium and calcium oxide in the gas phase is more than six orders of magnitude less than the concentration of anhydrite or solid calcium oxide.

The dehydration of calcium sulfate is an interesting case of water remaining in a compound well above the normal boiling point of water. Figure 28 illustrates the low-temperature portion of Figure 27 in more detail, where the formation of a residual mildly hydrated sulfate is predicted to persist to temperatures that exceed the normal boiling point of water. This is an indication of relatively strong bonding of the water to the sulfate.

Most species are more complicated in their decomposition than is gypsum. One important example is illite. Illite itself is a problematic species in that it has a relatively broad range of chemical compositions. In this sense, it is only marginally a stoichiometric species in the normal

Figure 27 Thermal decomposition of hydrated calcium sulfate (gypsum) during particle heating.

Figure 28 Dehydration of gypsum to produce anhydrite with residual hydrated sulfate persisting to significant temperature.

sense of the word. It represents one of the most important components of coal, however. There are theoretically consistent ways to deal with the stoichiometric variabilities of illite, but they take some time to discuss. Rather than diverge into such a discussion, we use muscovite as a surrogate for illite in that it undergoes most of the same transformations. The primary difference between them is that muscovite contains more aluminum than does illite.

Figure 29 illustrates the thermal decomposition and reaction of muscovite during rapid particle heating. Unlike gypsum, muscovite begins forming liquid phases at relatively low temperatures (about 810 °C) and decomposes into many separate species. The low melting behavior of illite (compared to kaolinite) is related to the formation of alkali alumino-silicates during decomposition. The relatively low melting temperature of these alkali-silicates is largely responsible for the plastic nature of boiler ash deposits. That is, the molten phase binds solid particles together and forms a deformable mass that is characteristic of deposits from high-rank coals.

Figure 29 Reactions of illite (represented here by muscovite) during rapid heating.

By contrast, kaolinite decomposition (Figure 30) forms essentially no liquid phases until very high temperatures. The dehydration of kaolinite leads to oxide and silicate formation at relatively low temperatures, but the oxides and silicates do not melt until quite high temperatures.

Finally, pyrite decomposition is an important feature of coal combustion. This is illustrated in Figure 31. In this case, pyrite loses sulfur to form pyrrhotite, which melts at relatively low temperatures. Some oxidation of both the pyrite and the pyrrhotite are indicated, but this mineral

grain is embedded in a coal particle and is not exposed to significant oxygen concentrations during most of its residence time in the boiler. Hence only Wuestite (FeO) is formed during oxidation.

Figure 30 Kaolinite decomposition as a function of temperature.

Figure 31 Decomposition and oxidation of pyrite during typical combustion conditions.

The formation of liquid pyrrhotite is largely responsible for the enrichment of iron in lower furnace deposits that is often observed in boilers. The pyrrhotite particles melt almost completely and reduce the rebound energy of the overall fly ash particle when striking a surface. This leads to adhesion of the particle on the surface. Since this mechanism is specific to pyrite, and since most of the iron in most high-rank coals is in the form of pyrite, an overall enrichment of iron in the deposit is observed. This enrichment leads to lower melting temperatures of the slag than of the ash formed from the fuel, since iron is an effective fluxing agent for most silicate fusion reactions.

These are representative results for some of the most important species in coal ash. All of these predictions are qualitatively correct and most are probably quantitatively correct. However, several caveats need to be made about these predictions. Most significantly, the predictions depend in part on thermodynamic properties from the literature. We have documented many errors in such available data from even the most trusted sources, including widely circulated handbooks, journal articles, and electronic databases. Unfortunately, the most trusted sources tend to focus on gaseous data from hydrocarbon fuels, not on inorganic condensed phases. However, even highly reputable sources contain many errors. We are working through a set of coefficients for species that we believe to represent a reasonable basis set for inorganic material in coal, but this is a difficult and time-consuming effort.

Secondly, even in the presence of perfect heat capacity and reference data, transport effects and kinetics play a large role in many of these predictions. The transport and kinetic constraints are not well characterized. These constraints are of minor consequence to single species decompositions as have been illustrated here. However, they probably dominate the transformations that occur in deposits as they reside on heat transfer surfaces.

The types of data indicated previously are summarized in Figure 32 for several of the most important inorganic species. Melting temperatures for all but illite, biotite and pyrite generally exceed 2552°F. (1400°C.), which is a reasonable upper bound for deposit temperatures in all but the most intense radiative zones of pc boilers.

Figure 32 Phase transformations of minerals commonly found in coal.

5. Deposit Formation

Ash Deposition: A Brief Overview

Significant experimental and theoretical work has been directed at developing a better understanding of ash deposition and the resulting deposit properties during coal combustion. Quantitative data addressing deposit properties as a function of coal (and other fuel) properties, location within an experimental facility, and operating conditions have been published by several investigators [Chow and Lexa 1987; Griffith, Lexa et al. 1988; Durant, Kwasnik et al. 1989; Loehden, Walsh et al. 1989; Baxter 1990; Baxter 1990; Baxter, Hencken et al. 1990; Harding and Mai 1990; Srinivasachar, Helble et al. 1990; Srinivasachar, Helble et al. 1991; Baxter and Jenkins 1995; Baxter, Jenkins et al. 1995; Baxter and Chigier 1996; Baxter, Jenkins et al. 1996; Baxter, Miles et al. 1996; Baxter, Blander et al. 1997; Baxter, Gale et al. 1997; Baxter, Miles et al. 1997; Baxter and Nielsen 1997; Baxter, Robinson et al. 1997]. However, there are fewer published ash deposition data from facilities larger than pilot scale.

A great deal of information is available on rates and mechanisms of ash deposition. In our work, we consider four major mechanisms of deposition, or mass transport to a surface: (1) inertial transport including impaction and sticking, (2) thermophoresis, (3) condensation, and (4) chemical reaction. In general, the rates of inertial impaction on cylinders in cross flow are well established. Rates on walls with parallel flows are less well established. The capture efficiency, a measure of the propensity of material to stick to a surface upon impaction, is far less well established. The rates of thermophoretic deposition are reasonably well established when local temperature gradients and the functional form of the thermophoretic force on the particle (or the thermophoretic velocity) are known. Condensation rates can be predicted reasonably well given accurate vapor pressure and concentration data. The accuracy to which rates of chemical reaction are known is often inadequate, especially those involving sulfation and alkali adsorption in silicates.

The results discussed below rely in part on an engineering model that predicts relevant aspects of ash deposition in pulverized coal boilers [Baxter, Fletcher et al. 1988; Baxter 1992; Baxter and Dora 1992; Baxter 1993; Baxter and DeSollar 1993; Baxter, Gale et al. 1997]. An engineering model called ADLVIC (Ash Deposit Local Viscosity, Index of refraction, and Composition) was initiated under DOE/FE sponsorship that contained most of this information. A model tentatively named TADIM (Transformations and Deposition of Inorganic Material) is now being developed under EPRI-sponsorship and features more technical detail, a much more friendly user interface, modern object-oriented design, and on-screen graphical output. This model is based on both first-principle derivations and a series of experimental results, supplementary to those indicated in the references above, that allow specification of critical parameters in the mechanisms of ash deposition. Over a dozen predictions from this model have been compared with experimental results from combustion systems of several different sizes and coals of many different ranks.

In this report, we summarize and compare the properties of coal as they pertain to ash deposition, describe the methodology incorporated in ADLVIC and TADIM for predicting ash deposition,

and outline the influence of inorganic material in its varied forms on ash deposit properties. Much of this discussion is relevant in analyzing high temperature corrosion, degradation of ceramic material in combustion environments, and other combustor-surface-related issues.

Mechanistic Description of Ash Deposition

The primary mechanisms of ash deposition are briefly reviewed here, followed by some examples of their use in predicting ash deposition rates. A more quantitative and detailed analysis of these rates is presented later in this document. In this latter discussion, the details of the formulations, their sensitivity to assumptions, and their general accuracy are described at a level of detail proportional to the importance of each mechanism to the overall process.

Both ash deposition rate and the properties of ash deposits are important considerations in the operation of a coal-fired combustor. The properties of ash deposits most important to the successful operation of a combustor include: (1) the ease of removal from a combustor surface (this is referred to as the deposit tenacity); (2) viscosity; (3) effective thermal conductivity; (4) effective emissivity; and (5) deposit strength (this reflects strength of the bulk material, as opposed to tenacity). Additional deposit properties, whose importance may be less obvious to the operator, but which strongly influence properties 1-5 above include: (6) elemental composition; (7) morphology; (8) porosity; and (9) chemical species composition.

The discussion in the previous section briefly outlined the transformation of inorganic material during combustion. The discussion below focuses on deposition and the connection between deposit properties (and rate of accumulation) and fuel properties. This relationship depends strongly on combustor type, location within the combustor, and operating conditions. The relationship also depends on what is termed a mineralogical description of the inorganic material. The term mineralogical is used in a broad sense that includes the specification of atomically dispersed material (that is not actually mineral in a strict sense) and granular material of a true mineral nature.

It is significant that a mineralogical description of the inorganic material in the coal is required, as opposed to an ASTM ash analysis. ASTM procedures can be used to generate much of the required information. For example, pyritic sulfur can be used to quantitatively estimate the fraction of pyritic iron in the coal, and free silicon (silicon in the form of silica) can be estimated from the ratio of silicon to aluminum in the ash. Other coal mineralogies cannot be easily estimated from ASTM procedures. Principal among these are calcitic calcium, atomically dispersed species of any type, and the precise composition of silicates. The behavior of different minerals with similar elemental composition varies markedly. For example, the behavior of a mixture of silica and alumina has little resemblance to that of an alumino-silicate.

Frame of Reference

The frame of reference for this discussion is that of inorganic material traveling through a combustor from its injection to its removal. The inorganic material responds to the changing environment encountered along this path. These changes are cast in the form of a series of coupled, ordinary differential equations, the solutions to which indicate temperature, velocity, and position of the material as a function of its residence time. Also included in these equations

is the rate of accumulation of ash on combustor surfaces. The solutions to the differential equations are used to predict the rate of deposition and deposit properties.

The four processes that principally contribute to deposit formation are: (1) inertial impaction (and particle capture), (2) thermophoresis, (3) condensation, and (4) heterogeneous reaction. To these four principal processes, we would add the process of eddy impaction, which is more difficult to capture mathematically, but which is of significance to flows with high concentrations of fume particles.

These processes are assumed to have additive influences on the total deposit mass. That is, the mass rate of deposition of ash at residence time t is given by

$$\frac{dm_i}{dt} = I_i(\tau, t)G_i(\tau, t) + E_i(\tau) + T_i(\tau, t) + C_i(\tau, t) + R_i(\tau, t) \quad (12)$$

In this equation, m_i represents the mass of component i in the deposit. The factor I_i represents the rate of inertial impaction, G_i the particle capture efficiency, E_i the eddy impaction rate, T_i the rate of thermophoretic deposition, C_i the rate of condensation, and R_i the rate of chemical reaction. The subscript i refers to each of the inorganic components in the raw coal. These include, for example, pyritic iron, other forms of iron, silica, silicates, calcite, atomically dispersed species (sodium, calcium, potassium, magnesium, and titanium), etc.

The variable t is a material time scale, designating residence time relative to the time of injection of the coal particle into the combustion environment. It typically varies between 0 and 3 seconds. The variable τ designates elapsed or laboratory (clock) time, i.e., time relative to an arbitrary time of day independent of the residence time. It represents, for example, the time between soot blowing cycles in the boiler and typically varies between 0 and 20 hours. In a steady-state or stationary system, the only relevant time scale is t and ash deposition rates, composition, and all other characteristics of the process have the same mean values at all times at a given location. However, ash deposition clearly is a non-stationary process [Baxter, Hencken et al. 1990]. Therefore, both the material and elapsed time scales must be addressed. Equation (12) can be thought of as an ordinary differential equation parameterized by the variable τ .

Practical illustrations can be used to clarify the differences in the two time scales. Changes in deposit composition from one location to another in a coal combustor are indicative of variation of one or more of the terms in Equation (12) with particle residence time (t). For example, commercial and pilot scale observations indicate that ash deposits formed from eastern and midwestern, pyrite-bearing coals are enriched in iron. This enrichment is most pronounced when the deposits are sampled near the burners, with typical enrichments of 60 %. Deposits sampled midway between the burners and the furnace exit are slightly less enriched in iron. A typical enrichment of 40 % may be observed in this area. Near the furnace exit, iron enrichment in the deposit drops to 10 to 20 %. This change in deposit composition with location is a reflection of the residence time (t) dependence of the inertial impaction and particle capture efficiency terms in Equation 12.

Changes in deposit composition as a function of deposit thickness are indicative of variation of one of the terms in Equation (12) with clock time (τ). For example, deposits formed in the convection pass of boilers typically show pronounced variation in composition between the combustor surface and the outside of the deposit. These composition changes are often associated with variation in the condensation rate with τ . As the deposit accumulates, its surface temperature increases and the rate of condensation decreases.

Each of the major mechanisms of ash deposition indicated in Equation 12 is conceptually reviewed below. A cylinder in cross flow is used to illustrate several of the mechanisms, although the same mechanistic processes describe deposition on both cylinders and walls.

Inertial Impaction $I(t, \tau)$

Inertial impaction (see Figure 33) is most often the process by which the bulk of the ash deposit is transported to the combustor surface. Particles depositing on a surface by inertial impaction have sufficient inertia to traverse the gas stream lines and impact on the surface. The particle capture efficiency describes the propensity of these particles to stay on the surface once they impact. The rate of inertial impaction depends almost exclusively on target geometry, particle size and density, and gas flow properties. The capture efficiency depends strongly on these parameters and on particle composition and viscosity [Srinivasachar, Helble et al. 1990; Srinivasachar, Helble et al. 1991; Srinivasachar, Senior et al. 1992]. It also depends on deposit surface composition, morphology, and viscosity [Smouse and Wagoner 1991; Wagoner and Yan 1991].

Figure 33 Conceptual illustration of inertial impaction mechanism on a cylinder in cross flow. One rebounding and one sticking particle are also illustrated.

The relative magnitudes of the characteristic times and dimensions of particle and fluid relaxation processes control the rate of inertial impaction. Specifically, inertial impaction occurs when the distance a particle travels before it fully adjusts to changes in the fluid velocity is larger than the length scale of an object, or target, submerged in the fluid. The particle Stokes number is defined as the ratio of these two length scales.

Inertial impaction is illustrated schematically in Figure 33 for the case of a cylinder in cross flow. Two particles are illustrated as they approach the cylinder. Both respond to the gas flow field around the cylinder by beginning to move around the cylinder on approach. The inertia of both particles overwhelms the aerodynamic drag forces, and they impact on the cylinder. One is shown rebounding and the other sticking to the surface. Gas stream lines, including recirculation zones, are shown in light gray.

This process is most important for large particles (10 μm or larger) and results in a coarse-grained deposit. The impaction rates are highest at the cylinder stagnation point, decreasing rather rapidly with angular position along the surface as measured from this stagnation point. At angular displacements larger than about 50° (as measured from the forward stagnation point), the rate of inertial impaction drops to essentially zero under conditions typical of combustor operation.

The particle capture efficiencies can be estimated from global empirical correlations based on particle residence time and composition. The product of the capture and impaction efficiencies yields the collection efficiency. Therefore, the deposition rate of each inorganic component on the surface is directly proportional to its capture efficiency. There are wide variations in capture efficiency among different chemical components.

The impaction efficiency is indicated in Figure 34 and is defined as the ratio of number of particles that impact the tube surface to the number that are directed at the tube in the free stream. Predictions of the impaction efficiency as a function of particle, gas, and tube properties have been published, at various levels of approximation, by numerous investigators [Laitone 1981; Beer and Chigier 1983; Israel and Rosner 1983; Rosner 1989; Rosner and Tassopoulos 1989; Baxter, Abbott et al. 1991; Baxter and DeSollar 1991]. The figure indicates that inertial impaction can be characterized as a function of the particle Stokes Number, which is defined for a cylinder in cross flow as

$$St^c \equiv \frac{\rho_p d_p^2 \langle u_p \rangle}{9\mu_g d_c} \Psi \quad (13)$$

where ρ_p , d_p , and $\langle u_p \rangle$ represent particle density, diameter, and mean velocity, respectively, and μ_g and d_c represent gas viscosity and tube diameter, respectively. Ψ is a correction factor that is only important when the particles do not obey Stokes' law, i.e., large particles with high velocities relative to the gas. Under typical conditions at the entrance of a convection pass (gas temperature 1580 K, gas velocity 16 m/s, tube diameter 7.62 cm or 3 in, particle specific gravity

= 2), a 40 μm particle ash particle has a Stokes Number of about 1.2 and a 10 μm particle has a Stokes number of approximately 0.07. Further investigation of the influence of the boundary layer, thermophoresis, and turbulence on this impaction efficiency is discussed elsewhere [Baxter 1990; Baxter and Hardesty 1990; Sinquefield, Baxter et al. 1998].

Figure 34 Correlation of particle impaction efficiency on a tube in cross flow as a function of Stokes number. Points and functions designated R are from the literature [Israel and Rosner 1983; Baxter and Hardesty 1990].

Thermophoresis $T(t, \tau)$

Thermophoresis is a process of particle transport in a gas due to local temperature gradients. Under some circumstances, thermophoretic deposition accounts for a dominant fraction of the submicron particulate on a surface. Under most conditions relevant to coal combustion, however, the other mechanisms of deposition contribute a larger fraction of the total deposit mass than thermophoresis.

Thermophoretic forces on a particle may be induced either by the temperature gradient in the gas in which the particle is suspended or as a consequence of a temperature gradient in the particle itself [Fuchs 1964; Byers and Calvert 1969; Gökoglu and Rosner 1984; Gökoglu and Rosner 1985; Gökoglu and Rosner 1986]. The origin of thermophoretic forces on a particle can be appreciated from the following, overly simplified argument. A particle suspended in a fluid with a strong temperature gradient interacts with molecules that have higher average kinetic energies on the side with the hot fluid than on the side with the cold fluid. The energetic collisions of the high energy molecules on the hot side of the particle create a stronger force than those of the low energy molecules on the cold side. This gives rise to a net force on the particle. In general, these forces act in the direction opposite to that of the temperature gradient, although they can act in the direction of the gradient under certain conditions of particle surface temperature.

An illustration of thermophoretic deposition as it is manifest in coal combustion equipment is presented in Figure 35. Thermophoretic deposits are finer grained and more evenly distributed around the tube surface than deposits formed by inertial impaction, as indicated. With increasing deposit accumulation on the tube surface, there is a decrease in the temperature gradient in the thermal boundary layer, decreasing the rate of thermophoresis.

Figure 35 Schematic illustration of thermophoretic deposition on a tube in cross flow.

We have adapted a functional form for the thermophoretic force that should apply over a broad range of Knudsen numbers (ratio of the gas mean-free-path to the particle diameter). It is based on an integration of particle-gas momentum exchange over the surface of the particle [Jacobsen

and Brock 1965] and has been used by other investigators with some success [Im and Chung 1983]. The thermophoretic force, as used in this model, is given by

$$F_T = -6\pi\mu_g d_p f(Kn) \nabla T_g \quad (14)$$

where $f(Kn)$ depends on particle diameter, Knudsen number, and several material-specific properties. Further discussion about thermophoresis is included elsewhere [Baxter and Hardesty 1990; Baxter and Hardesty 1992; Baxter and Hardesty 1992].

Condensation $C(t, \tau)$

Condensation is the mechanism by which vapors are collected on surfaces cooler than the local gas. An illustration of deposition by condensation on a tube in cross flow is presented in Figure 36.

Figure 36 Schematic illustration of condensation on a tube in cross flow.

The amount of condensate in a deposit depends strongly on the mode of occurrence of the inorganic material in the coal. Low rank (subbituminous) coals, lignites, and other similar fuels have the potential of producing large quantities of condensible material. Furthermore, the role of condensate in determining deposit properties can be substantially greater than the mass fraction of the condensate in the deposit might suggest. For example, condensate increases the contacting area between an otherwise granular deposit and a surface by several orders of magnitude. This increases by the difficulty of removing the deposit from the surface by a similar amount. Condensate can also increase the contacting area between particles by many orders of magnitude, having profound influences in the bulk strength, thermal conductivity, mass diffusivity, etc. of the deposit. Condensation is a relatively minor contributor to the development of deposits and

their properties for most high-rank coals. However, in lower grade coals (and fuels such as biomass) condensation becomes a significant contributor.

All vapors that enter the thermal boundary layer around a cool surface and subsequently are deposited on the surface can be thought of as condensate. Condensation occurs by at least three mechanisms: (1) vapors may traverse the boundary layer and heterogeneously condense on the surface or within the porous deposit; (2) vapors may homogeneously nucleate to form a fume and subsequently deposit by thermophoresis on the surface; and (3) vapors may heterogeneously condense on other particles in the boundary layer and arrive at the surface by thermophoresis [Rosner and Nagarajan 1985; Helble, Neville et al. 1986; Castillo, W.Mackowski et al. 1990].

Condensation deposits have no granularity at length scales larger than $0.5 \mu\text{m}$ and are more uniformly deposited on the tube than either thermophoretically or inertially deposited material. The deposits are tacky and have a strong influence on the surface capture efficiency. The condensation flux is described by the following equation

$$C_m = \zeta_m \theta (x_{m,b} - x_{m,s}) + x_{m,b} \sum_i C_i \quad (15)$$

where ζ_i is the condensation efficiency, θ is a blowing factor (which will be very near unity for this application), k_m is a mass transfer coefficient (that depends in known ways on geometry, Reynolds number, and fluid properties), and x represents a mole fraction of species i in the bulk gas (subscript b) and at the tube surface (subscript s). The second term on the right side of the equation represents convective transport to the surface.

Chemical Reaction $R(t, \tau)$

Inertial impaction and thermophoresis describe the two most significant mechanisms for transporting particulate material to a surface. Condensation involves transportation of vapors to a surface by means of a physical reaction and phase change. Chemical reactions are the fourth of the principal mechanisms by which mass can be accumulated in a deposit (see Figure 37). These involve the heterogeneous reactions of gases with materials in the deposit or, less commonly, with the deposition surface itself. Some of the chemical species found in deposits are not stable at gas temperatures, alkali sulfates being typical examples. The sole source of these species is heterogeneous reactions between gas phase constituents and constituents of the lower temperature deposits.

Among the most important chemical reactions with respect to ash deposition during coal combustion are: (1) sulfation, (2) alkali absorption, and (3) oxidation. The principal sulfating species of concern are compounds containing the alkali metals, sodium and potassium. Sodium and potassium in the forms of condensed hydroxides and possibly chlorides are susceptible to sulfation.

Silica absorbs alkali material to form silicates. Silicates are less rigid and melt at lower temperatures than silica. The transformations of silica to silicates in deposits can induce sintering and significant changes in deposit properties. These reactions are relatively slow compared to sulfation.

Figure 37 Schematic illustration of chemical reaction on a tube in cross flow.

Residual char often deposits with the inorganic material on combustor surfaces. However, the char oxidizes with locally available oxygen to produce deposits with very little residual carbon. In coal combustion, carbon typically accounts for less than 2 % of the overall deposit mass.

Chemical reactions, such as sulfation of alkali species and combustion of residual carbon in the ash, are similar to condensation in their mathematical treatment [Baxter and Hardesty 1990]. Both condensation and chemical reactions are strongly temperature dependent and give rise to spatial variation in ash deposit composition.

Eddy Impaction $E(t, \tau)$

Eddy impaction is a fifth process by which particles too small or light to inertially impact arrive at surfaces. They are deposited by the actions of turbulent eddies within or near the boundary layer rather than solely by their inertia as in inertial impaction. This process is less well understood than any of the previously discussed processes, and its description is tied to largely empirical coefficients. It influences only relatively small particles.

Ash Deposition in Practical Systems

The analysis of deposit growth and property development discussed in the preceding sections can be formalized as a deposition model. This model, called ADLVIC, has been developed and applied to a large number of pulverized-coal-fired combustors with differing coal types and operating conditions. The following discussion highlights results from one pilot-scale and one utility-scale combustor for coals burning eastern and western coals, respectively. The experimental facilities are first briefly introduced, followed by a comparison of predicted and measured results.

The Multifuel Combustor (MFC), at Sandia's Combustion Research Facility, is used to collect fundamental data to validate the model at pilot scale under well controlled and characterized conditions. The MFC data provide details of time dependencies of the process and can be sampled under a larger variety of operating conditions than is feasible for utility-scale combustors. The addition to MFC data, data were obtained during field tests in a 600 MW_e utility boiler owned and operated by Central Illinois Public Services (CIPS) and were used to validate the model at utility scale under typical industrial conditions. The CIPS experiment involved predicting the ash-related behavior associated with switching fuel from their typical eastern/midwestern supply to a Wyoming coal. Several other utilities have attempted similar fuel switches, most typically creating severe ash-related problems with the western fuels. The MFC was previously described. The utility boiler is described in more detail below.

Utility Boiler (CIPS)

The utility boiler used in this study is a 600 MW_e unit (see Figure 38) operated by CIPS with no slagging and/or fouling load restrictions when burning the traditional coal. It is a tangentially fired unit with a maximum continuous rating (MCR) coal feed rate of 235 tons/hr. The boiler is 61 feet wide, 52 feet deep, and 195 feet high with 100,000 sq. ft. of heat transfer surface and a total furnace volume of 516,000 cubic feet. Six levels of adjustable burners feed coal from each of the corners of the furnace box. The economizer is constructed of spiral loop finned tubes. This unit was designed to burn a local coal. However, the results discussed here are from a three-week test burn of a Wyoming (Hanna Basin) coal during which approximately 72,000 tons of coal were consumed. Additional details about the unit are available elsewhere [Baxter and Hardesty 1990].

During the test burn, ash deposits were sampled at the boiler nose for comparison to model predictions. Ash deposits at other locations in the boiler were not accessible for on-line sampling. At the conclusion of the test burn, a boiler inspection was performed and samples of deposit were collected throughout the boiler, as indicated by the circles in the diagram. Photographs of ash deposits at the same locations were obtained, and several bulk deposits from the boiler were collected to study deposit morphology. Elemental composition was determined for each of the samples for comparison to model predictions. Composition was determined for the bulk deposit. Variations in deposit composition with distance from the heat transfer surface were not determined. The deposit properties depend on both the composition of the material being deposited and on the relative rates of the various mechanisms by which they are deposited.

Figure 38 A cross-sectional view of the CIPS 600 MW_e unit used in performing a test burn of the Wyoming coal. Circles indicate locations from which ash deposits were sampled after the test burn.

Comparison of Experimental Results with Predictions

The following qualitative and quantitative comparisons of predictions with experimental results are based on the original model (ADLVIC) and are presented as illustrations of expected performance from TADIM. TADIM includes all of the mechanisms described by ADLVIC with many additional improvements and we expect that TADIM will compare at least as well. However, we have not performed comparisons of TADIM predictions with data yet.

Some of the properties of deposits can be quantified by standardized measurement techniques. The most common example is the elemental composition of the ash, which is normally reported on the basis of the oxides of the major species in the ash. Most deposit properties of interest to operators and designers of facilities (a) do not have any metrics for comparison, (b) have metrics that are not standardized, or (c) are very seldom measured in utility boilers. Examples include deposit tenacity (sometimes called removability or cleanability), strength, morphology, emissivity, rate of growth, etc. This latter group of properties are typically reported in qualitative or comparative terms.

Qualitative Predictions and Observations

Rate of Deposition: Experimental results indicate that char particle fragmentation is more substantial for the cenosphere-forming bituminous coals than for subbituminous or lignite coals [Baxter 1992]. Therefore, the rate of *impaction* of particles on the tubes for the Wyoming coal is predicted to be higher than for the bituminous coal normally used in the boiler due to the size distribution of the fly ash. However, the subbituminous-coal fly ash contains a higher proportion of constituents with low *capture efficiencies* than the bituminous-coal fly ash. On balance, the rate of accumulation was qualitatively predicted to be about the same for the Wyoming coal as for the coals previously used in the boiler. Note that under different conditions, similar coals behave quite differently in boilers designed to burn eastern fuels (see, for example, [Ziesmer, Barna et al. 1990]).

The observed rate of deposition during the test burn is consistent with the predictions discussed above. The rate of deposit accumulation was about the same, perhaps slightly slower, than that experienced with previous bituminous coals in this boiler under similar operating conditions.

Morphology and Strength: The Wyoming coal contains a relatively high proportion of free silica compared to other coals of similar rank, ash chemistry, and geographical origin. The free silica particles are slow to fuse or sinter in the deposit and contribute to both the granular, porous nature and the lack of deposit strength. This high percentage of free silica is also largely responsible for the high ash fusion temperatures of this coal compared to other similar coals. A second major contribution comes from the calcite. Calcium that originates as calcite (as compared to organically bound or siliceous calcium) has an effect similar to free silica on the deposit with respect to granularity and deposit strength, although less pronounced. Finally, this particular boiler has a generously sized radiant section and was operated with a furnace exit gas temperature somewhat lower than many boilers. The lower temperatures in the top portion of the radiant section helped to condense and solidify vapors before they reached the convection pass. The condensed, solidified vapors are particles and do not enhance deposit strength significantly.

Vapors that condense in or on the deposit are largely responsible for enhancing deposit strength by increasing the density and the contacting area between particles.

The observed morphology, density, porosity, and strength of the deposits is consistent with the predicted results. Specifically, the deposits were granular, friable, and showed no indication of significant sintering.

Utility experience typically is the opposite of this observed trend when switching to coals similar in geographic origin and organic composition to the Wyoming coal used in this test [Ziesmer, Barna et al. 1990]. This illustrates the need to consider mineralogy, operating conditions, and boiler type when predicting ash deposition behavior.

Removability: Sintering and fluid formation in these coals is often associated with (a) the incorporation of alkali material in silica to form low-melting-point silicates and (b) sulfation of sodium or calcium on the relatively cool surface. We predicted a lack of sintering or fluid formation based on our experience with other coals in MFC tests and the mineralogy of the Wyoming coal. Deposits generated from Wyoming-type coals that produce sintered deposits typically are associated with deposits that have relatively high sodium and/or high sulfur contents relative to the ash content. The Hanna Basin coal has a modest amount of atomically dispersed (condensable) sodium and a low ratio of sulfur to total ash compared to other western coals. Therefore, we predicted little sintering or formation of fluid phases.

During the three-week test burn in the 600 MW_e boiler, deposits were easily removed using standard maintenance procedures, consistent with the anticipated behavior. There was no indication of fluid or condensed phases next to heat transfer surfaces.

Experience of many other utilities is opposite to that observed and predicted here when they performed similar tests with similar coals. Western coals often form sintered deposits in utility boilers [Ziesmer, Barna et al. 1990]. This underlines again the dependence of deposit properties on boiler geometry, boiler operating conditions, and coal mineralogy and the inability to predict deposit properties on the basis of fuel properties alone.

Emissivity: We also anticipated that the deposits will have a high reflectivity based on the relatively high deposition rates of calcium and the low deposition rates of iron. This is consistent with the observations during the test burn. During the test burn, the furnace exit gas temperature was about 100 °C above its typical value when burning bituminous coals (but still below that of many similar boilers), indicating higher ash reflectivity in the radiant section of the boiler.

Western coals are well known for the formation of reflective ash in the radiant section of the boiler. This prediction is consistent with the bulk of utility experience with western coals, regardless of the type of boiler used to combust the coal.

Quantitative Predictions and Experimental Results

Figure 39 illustrates predicted and measured ash deposit elemental composition as a function of particle residence time (*t*) [Baxter, Abbott et al. 1991; Baxter and DeSollar 1991] in the Sandia

MFC combustor. Replicate experiments indicate that the coefficient of variation (standard deviation divided by the mean) for these data is 6-7 %. For a typical pulverized coal boiler operating at maximum continuous rating, the data represent conditions near the burners at 0.15 s and near the furnace arch at 1.1 s residence time.

Figure 39 Comparison of sensitivity of data (symbols) and predictions (lines) to particle residence time for a Pittsburgh #8 coal. The dominant dependence in this particular case is the iron concentration. Data are from the MFC.

As indicated in the figure, the ash chemistry changes rapidly early in particle residence time. Later in residence time, changes in ash chemistry become less pronounced. These data are in qualitative and, in many cases, quantitative agreement with the predictions, including those elements in less than 2 % concentration in the ash (Figure 39b). They are also in agreement with general utility experience that iron is both predicted and measured to be enriched in the deposits at early residence time relative to late residence time.

Most currently employed indices of fouling and slagging are based on properties of the raw coal. There is no mechanism in such indices to predict different behavior in different regions of the furnace or in different regions of the convective pass. The data in Figure 39 illustrate how the deposit composition changes continuously through the boiler. These changes effect similar changes in deposit properties. This is illustrated in Figure 40, where deposit viscosity is shown as a function of temperature based on a published deposit viscosity model [Kalmanovitch and Frank 1988].

Figure 40 Deposit viscosity predicted from measured, predicted, and coal ash composition for the Pittsburgh #8 coal at 0.2 s residence time in the MFC. A notable improvement in the prediction is noted compared with the coal ash values.

Results are shown based on the composition of the raw coal, the predicted deposit composition, and the measured deposit composition. The results for the raw coal correspond to currently employed indices of ash behavior (which are based on coal rather than deposit composition). The figure illustrates both the agreement between predicted and measured values and the difference between them and the corresponding values for the raw coal. Similar plots will be used for other comparisons later in this discussion.

The predictions and measurements in Figure 39 and Figure 40 benefit from being conducted in a facility with well known and tightly controlled operating conditions. Utility boilers do not typically have such well controlled or characterized conditions. Comparison of predicted and observed deposit composition results from the CIPS boiler provides some indication of the practical usefulness of the model. During and after the test burn, deposits were sampled from several locations in the boiler, as indicated by the circles in Figure 38. Results from two of these regions are presented below.

Figure 41 and Figure 42 illustrate the predicted composition of deposits collected from the nose and economizer regions of the boiler. Particle residence times are estimated at 1.2 s and 1.9 s for the nose and economizer sections of the boiler, respectively. The data in Figure 41 represent the average of four replicate samples with a coefficient of variation of approximately 12 %. The data in Figure 41 were obtained during boiler operation. Samples from most of the other sampling locations in the boiler could not be obtained during operation and there was no opportunity to replicate them or do statistical analyses of the results. Based on the analysis of the data in Figure 41, some of the differences between the predicted and observed concentrations are larger than the uncertainty in the data. However, the data in both figures are in reasonable agreement and, for the most part, show consistent trends.

The viscosity of the deposits in the first superheater tube bank and in the economizer (both predicted as tubes in cross flow) is illustrated in Figure 43 and Figure 44. These figures indicate quantitatively that deposit properties cannot be reliably based on fuel properties without regard to the transformations and selective deposition that occurs during combustion. The improvement in predicting deposit properties by using the means discussed above is also indicated.

These comparisons indicate that quantitative predictions of ash deposit chemistry can be obtained with reasonable accuracy, even for elements with mass fraction less than 5 percent. This comparison of predicted and measured properties portends an ability to anticipate ash-related problems in combustors for a range of operating conditions, fuel types, and geometries. The eventual goal of this work is to provide predictions accurate enough that they can be used in the operation of existing systems and the design of new systems to avoid unmanageable deposits while responding to other requirements (steam rate, pollutant emissions, etc.).

Conclusions Regarding Deposit Formation Mechanisms

The deposition of inorganic material during coal combustion can be described as a process involving five general mechanisms, each with two time scales. The mechanisms include inertial deposition, thermophoresis, condensation, eddy impaction and chemical reaction. Both particle residence time and process (clock) time are important in each of the processes.

Figure 41 Comparison of predicted and measured deposit compositions near the boiler nose in the CIPS 600 MW_e utility boiler. Replicated experiments in this facility indicate a standard deviation of the data of less than eight relative percent for all oxide species.

Figure 42 Comparison of predicted and measured deposit compositions on economizer tubes in the CIPS 600 MW_e utility boiler.

Figure 43 Comparison of deposit viscosity as a function of temperature in the first superheater tube bank over the nose in the 600 MW_e CIPS boiler.

Figure 44 Comparison of deposit viscosity as a function of temperature in the economizer of the 600 MW_e CIPS boiler.

Chemical species of the inorganic material in the coal, as opposed to the elemental composition of the ASTM coal ash, determine many important deposition mechanisms and deposit properties. Other important variables determining deposit properties include operating conditions, and boiler geometry. Means of incorporating all of these variables into tractable engineering models for ash deposition during coal combustion have been developed. The application of the model to western coals is demonstrated.

Deposit properties can be anticipated with reasonable accuracy based on their elemental composition and the predicted rates of various deposition mechanisms. Deposit composition, morphology, removability, and emissivity can be inferred from the mechanistic details of the engineering model. This mechanistic approach to ash deposition has the potential of providing real-time, accurate estimates of deposit properties for use in designing and operating solid-fuel-fired combustors of many types.

6. Particle Transport Equations

The preceding conceptual discussion receives precise mathematical definition in this section. The momentum, energy, and mass transport affecting particles dictates particle physical state, chemical composition, and behavior. Quantitative means of modeling these phenomena are summarized here.

This section of the report summarizes only the transformation and combustion-related particle equations. Dispersion of particles in turbulent flows is an additional, fundamental consideration. The dispersion equations and the methods of relating their predictions to particle number concentration fields is discussed separately. This discussion appears after the deposit formation discussion. The deposit formation mechanisms all rely on particle number concentration as a first-order term.

The mathematical description of transformations can be accomplished by a series of ordinary, nonlinear, coupled differential equations that describe the history of a fuel particle as it passes through a combustor. The spatial variation in gas temperature, composition, velocity, radiative fields, etc. is presumed known. This discussion outlines the current framework of the model and the state of development.

The model is cast in a material or Lagrangian reference frame. Therefore, the particle is described from the perspective of an observer riding on the particle through the combustor. The changes in gas conditions (temperature, velocity, and composition) as the particle visits different regions of the combustor are required input parameters.

In a material reference frame, the independent parameters describing a particle are time and starting location. For a given starting location, the only relevant parameter for a specified particle is time. Therefore, the behavior of the particle should lend itself to description by appropriate ordinary differential equations describing momentum, heat, and mass exchange between the particle and its environment and the associated initial conditions. Also, the loss of particles to surfaces are described as sink terms in the total particle number balance. These equations are described below.

Indicial notation is used in all vector equations (particle velocity and position). Subscripts i , j , and k are reserved to indicate vectors or higher-order tensors in this notation. For example, Z_i represents the position vector. This notation will allow a mathematically consistent development of the equations, although it sometimes complicates or obscures the expressions. Subscripts other than i , j , and k do not indicate vectors. When one quantity has both vector subscripts and nonvector subscripts, the vector subscripts are listed first and separated by other subscripts with a semicolon. For example, $Z_{i;p}$ represents particle position.

Particle Trajectories

Changes in particle velocity are dominantly effected by drag between the particle and the gas and by gravity. The equation of motion for particles describes these changes and is well established:

$$m_p \frac{dv_{i,p}}{dt} = \frac{\pi}{8} d_p^2 \rho_g C_d S s_i + m_p g_i \quad (16)$$

where m_p is the instantaneous mass of the particle, $v_{i,p}$ is the particle velocity component in the i direction, t is time, d_p is particle diameter, ρ_g is gas density, C_d is the particle drag coefficient (which will be discussed in more detail later), S represents the (scalar) magnitude of the difference between the gas and particle velocity vectors, s_i is the (vector) difference between the gas and particle velocities, and g_i is the component of the acceleration of gravity in the direction of i . The parameter S is mathematically represented by

$$S = (s_i s_i)^{1/2} \quad (17)$$

and the lower-case s_i represents the difference in velocity vectors

$$s_i = v_{i,g} - v_{i,p} \quad (18)$$

where $v_{i,g}$ represents the gas velocity and $v_{i,p}$ represents the particle velocity, both with respect to an inertial frame of reference.

The particle drag coefficient C_d depends primarily on Reynolds number. The Reynolds number dependence is illustrated by the data in Figure 45 and is well established. Also shown in the figure are several correlations of the data. Three representative correlations from the literature are illustrated. These are sometimes inaccurate and in all cases do not span the Reynolds number range of interest in these calculations (0-600,000).

Figure 45 Comparison of literature data and correlations for the drag coefficient over the range of interest in this project

A correlation that is both accurate and spans the range of interest is given by a piece-wise polynomial fit of the data in Figure 45 as follows:

$$C_d^R = \exp\{a + b[\ln(Re)] + c[\ln(Re)]^2 + d[\ln(Re)]^3\} \quad (19)$$

where Re is the particle Reynolds number and a , b , c , and d are fitting parameters defined over selected ranges of Reynolds number as indicated in Table 10. The Reynolds number is defined by

$$Re \equiv \frac{d_p S}{\nu_g} \quad (20)$$

where ν_g is the gas kinematic viscosity and the other terms were defined previously. The viscosity, ν_g , is evaluated at film conditions, i.e., at the arithmetic average of the gas and particle temperatures.

Table 10 Parameters for the correlation describing the Reynolds number dependence of the particle drag coefficient (see Eq.(19)).

Reynolds Number Range*	a	b	c	d
$Re < 1.0 \times 10^{-7}$	3.17805	1.0	0.0	0.0
$1.0 \times 10^{-7} \leq Re < 50,000$	3.25106	-0.859574	0.0307015	0.00142183
$50,000 \leq Re < 400,000$	835.582	-220.398	19.3526	-0.566191
$400,000 \leq Re < 30,000,000$	-15.2045	1.46032	-0.0366222	0.0
$30,000,000 \leq Re$	-0.91629	0.0	0.0	0.0

* Last data point is at $Re = 3,000,000$

At low Reynolds numbers (less than 0.2), the drag coefficient becomes $24/Re$, a well established limit. The Reynolds numbers of particles in coal combustors exceed 1,000 only during particle injection. Therefore, the correlation of drag with Reynolds number should be well approximated by Eq. (19).

The remaining parameters in Eq. (16) are either predicted from other differential equations or are transport coefficients and physical properties. Particle position is determined by solving the differential equations

$$\frac{dz_{i,p}}{dt} \equiv v_{i,p} \quad (21)$$

These six equations (three represented by Eq. (16) and three represented by Eq. (21)) describe the multidimensional velocity and position histories of the particles. They complete the particle trajectory portion of the prediction.

Particle Energy (Heat) Transfer

Heat transfer to the particle occurs through convection with the ambient gas and radiation. Heat sinks and sources on the particle surface include heats of fusion and vaporization and heats of reaction, respectively. An enthalpy balance on the particle establishes the relative contributions of these heat transfer and generation mechanisms. The total change in particle enthalpy is given by

$$m_p \frac{d\hat{h}_p}{dt} = A_p h_m \theta_T (T_g - T_p) + \varepsilon \sigma A_p (T_r^4 - T_p^4) + \Delta h_x \frac{dm_p}{dt} - \hat{h}_p \frac{dm_p}{dt} \quad (22)$$

where

$$\hat{h}_p = \int_{T_o}^{T_p} c_p dT + \hat{h}_p^o \quad (23)$$

and c_p is the particle heat capacity, k is the convective heat transfer coefficient, θ_T is the heat transfer blowing parameter, T is temperature, σ is the Stefan-Boltzman constant, ε is the emissivity, and Δh_x is the mass-averaged heat of reaction for the particle. Temperatures with subscripts g , p , and r , represent gas, particle, and radiative temperatures, respectively. The first term on the right of Eq. (22) represents convective heat transfer, the second radiative heat transfer, the third heat sources and sinks associated with chemical or physical reactions, and the fourth changes in total enthalpy associated with changes in total mass.

The total particle heat capacity is the mass-weighted average of the component heat capacities

$$c_p = \sum_m \omega_m c_{p,m} \quad (24)$$

where ω_m is the mass fraction of species m in the particle.

The convective heat transfer coefficient is computed from a Nusselt number correlation as follows

$$Nu \equiv \frac{h_m d_p}{k_g} = 2.0 + 0.6 Re_p^{1/2} Pr_g^{1/3} \quad (25)$$

where k_g is the gas thermal conductivity and Pr_g is the gas Prandtl number. The Prandtl number is the ratio of the gas viscosity to the thermal diffusivity.

The thermal blowing factor, θ_T , is given by

$$\theta_T = \frac{\phi}{e^{\phi} - 1} \quad (26)$$

where

$$\phi = \frac{c_p^{og} \frac{dm_p}{dt}}{A_p h_m} \quad (27)$$

The enthalpies of the individual components are calculated as a function of temperature as follows:

$$\hat{h}_m = \int_{T_{ref}}^{T_p} c_{p,m} dT + \hat{h}_m^o \quad (28)$$

where

$$c_{p,m} = \frac{R_g}{Z_m} \sum_{i=0}^n a_i T^{i-2} \quad (29)$$

The constants a_i , used to fit Eq. (29) to available data over specified temperature ranges, with n commonly on the order of 7. This leads to

$$\hat{h}_m = \frac{R_g}{Z_m} \left[a_{0,m} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) + a_{1,m} \ln \left(\frac{T}{T_{ref}} \right) + \sum_{i=1}^{n-1} \frac{a_{i+1,m}}{i} (T^i - T_{ref}^i) + a_{i+1,m} \right] \quad (30)$$

where

$$\hat{h}_m^o = \frac{R_g}{Z_m} a_{i+1,m} \quad (31)$$

Data from many databases are available in a form that can be cast in terms of Eq. (29). However, the reliability of the data is not high in the cases of inorganic species. Some discussion of the impact of errors in these thermodynamic coefficients is included in the Appendix.

Heats of fusion and vaporization are determined by the difference in the enthalpies of the two components involved in the phase change at the temperature of the particle. Heats of reaction are determined by the difference in the enthalpies of the products and reactants involved in a chemical reaction at the temperature of the particle.

The particle enthalpy is determined by numerically solving Eq. (22). The particle temperature is determined by iteratively solving Eq. (23) for temperature given the enthalpy computed from Eq. (22).

In the predictions to date, constant heat capacities and emissivities are used for the particle independent of temperature and, in most cases of the inorganic components, independent of composition.

Particle Reaction and Mass Transfer

The particles, or at least portions of particles, undergo both physical and chemical reactions in the combustor. Physical reactions include melting, vaporization, and fragmentation. Chemical reactions include devolatilization and oxidation. These reactions and their incorporation into an integrated computer code are discussed below.

Phase Changes

The solids sublime and, if temperatures rise high enough, melt during the flight of the particle. The vapor pressures over the solid and liquid are commonly fit with the following equation (a generalized form of the Antoine Equation)

$$p_m(T_p) = a \exp \left[b + \frac{c}{T_p} + d \ln(T_p) + e T_p \right] \quad (32)$$

where p_m represents the vapor pressure of component m , T_p represents the absolute particle temperature, and the remaining five parameters (a , b , c , d , and e) are used to fit available data. The general form of this equation is derivable from the Clausius-Claperyon equation and the coefficients b through e can be related to the heat capacity coefficients in Eq. (29). This is an efficient and generally accurate means of computing the vapor pressure, but it requires additional data for each species and may yield results that are incompatible with other thermodynamic properties. The additional data are difficult to find for inorganic species and are more difficult to validate. Incompatibilities of consequence to these calculations include determination of the normal boiling point, which should be the point at which the vapor pressure is 1 atm as predicted by Eq. (31) and the point at which the Gibbs free energies of the liquid and vapor phases are equal. The Gibbs free energy of a component is defined by

$$g_m(T, P) \equiv h_m(T, P) - T s_m(T, P) \quad (33)$$

where the enthalpy and entropy are determined from the (already required) heat capacities and reference properties.

The entire equilibrium vapor pressure curve for a species can be determined from the heat capacity and reference enthalpy data from the Clausius-Claperyon equation, which is a first-principles relationship between vapor pressures and thermodynamic properties.

$$\frac{dp_m}{dT} = \frac{\Delta h_{m,vap}}{T \Delta v_m} \quad (34)$$

where $\Delta h_{m,vap}$ is the heat of vaporization and Δv_m is the difference in specific volumes of the vapor and condensed phase. Vapors generally have specific volumes about 1000 times larger than the condensed phase and are generally well described by the ideal gas law. Neglecting the condensed-phase specific volume relative to that of the vapor in computing Δv_m and applying the ideal gas law for the vapor specific volume, this equation can be approximated as

$$\frac{1}{p_m} \frac{dp_m}{dT} = \frac{d \ln(p_m)}{dT} \approx \frac{\Delta h_{m,vap}}{R_g T^2} \quad (35)$$

Using Eq. (30) to express the enthalpy leads to

$$\Delta h_{m,vap} = R_g \left[\Delta a_{0,m} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) + \Delta a_{1,m} \ln \left(\frac{T}{T_{ref}} \right) + \sum_{i=1}^{n-1} \frac{\Delta a_{i+1,m}}{i} (T^i - T_{ref}^i) + \Delta a_{i+1,m} \right] \quad (36)$$

meaning

$$\frac{d \ln(p_m)}{dT} \approx \frac{\Delta a_{0,m} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) + \Delta a_{1,m} \ln \left(\frac{T}{T_{ref}} \right) + \sum_{i=1}^{n-1} \frac{\Delta a_{i+1,m}}{i} (T^i - T_{ref}^i) + \Delta a_{i+1,m}}{T^2} \quad (37)$$

This yields

$$\begin{aligned} \ln \left(\frac{p}{p_0} \right) \approx & \Delta a_0 \frac{T T_0 (T - T_0) + 0.5 T_{ref} (T_0^2 - T^2)}{T^2 T_0^2 T_{ref}} + \\ & \Delta a_1 \frac{T \left[1 + \ln \left(\frac{T_0}{T_{ref}} \right) \right] - T_0 \left[1 + \ln \left(\frac{T}{T_{ref}} \right) \right]}{T T_0} + \Delta a_2 \left[T_{ref} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \ln \left(\frac{T}{T_0} \right) \right] + \\ & \sum_{i=1}^{n-3} \frac{\Delta a_{i+2}}{i + i^2} \frac{T T_0 (T^i - T_0^i) + T_{ref}^{i+1} (T_0 - T)}{(i + 1) T T_0} + \Delta a_n \left(\frac{1}{T_0} - \frac{1}{T} \right) \end{aligned} \quad (38)$$

where p_0 is taken as 1 atm with the corresponding T_0 determined by determining the temperature where vapor and condensed phase Gibb's free energies (Eq. (33)) are equal. This equation requires no new coefficients. That is, the coefficients. The assumptions in the equation include (1) the condensed-phase specific volume is negligible compared to that of the vapor phase, and (2) the vapor obeys the ideal gas law. Both assumptions are accurate at regions far from the critical point and at modest pressures. However, the equation is somewhat more complicated than the Antoine equation and other correlating equations, although it has a similar basic form.

Partial pressures at the interface between the gas and condensed phase are assumed to equal the equilibrium vapor pressures during mass transport. The partial pressures are divided by the total pressure and multiplied by the fraction of the total volume occupied by each component to obtain mole fractions of vapor components at the particle surface in the gas. These mole fractions are used to model the rate of mass loss by vaporization, as described below.

The melting points and boiling points of the condensed-phase materials are determined by equating the Gibb's free energies (Eq. (33)) in the two phases involved. At these phase transitions, the relative amounts of the two phases are determined by an enthalpy balance. The

total particle enthalpy, which is predicted independently as discussed earlier, is related to the enthalpy of each particle component at the melting/boiling temperature through the following equation

$$h_p(T_p) = m_p \sum_{m=1}^L \omega_m \hat{h}_m(T_p) \quad (39)$$

where h_p is the total particle enthalpy, L is the total number of particle species/components, ω_m is the mass fraction of component m , and $\hat{h}_m$ is the specific enthalpy of component m . At phase transition temperatures, the mass fractions of the two phases involved in the transition are adjusted until Eq. (39) is satisfied.

Fragmentation

Char particle fragmentation is modeled by decreasing the diameter of the particles and increasing their number at a specified point in the particle mass history as determined by the daf mass loss. Each of the resulting fragments is assumed to have the same composition, diameter, temperature, etc. The parameters used in this fragmentation model are taken more or less directly (with some data smoothing) from the experimental work conducted under this project [Baxter 1992]. This work is published in the archival literature and not further summarized here. However, its major conclusions include: (1) char fragmentation is a minor contributor to fly ash number populations for most coal particles; (2) large ($> 80 \mu\text{m}$), cenosphere-forming (hvy bituminous coal) char particles may fragment significantly; and (3) the extent of fragmentation increases with decreasing ash loading and increasing initial char particle size.

Oxidation and Mass Transfer Rates

The rate of oxidation is determined by a combination of chemical kinetics and mass transport. These two rates of particle reaction are discussed here.

The rate of mass transfer to the particle is described by the following equation

$$N_m = \theta_m f_m (x_{m,s} - x_{m,b}) + x_{m,s} \sum_{m=1}^L N_m \quad (40)$$

where N_m is the molar flux of component m away from the particle, θ_m is the blowing factor which is defined later, f_m is the molar transfer coefficient which is also defined later, x_m is the mole fraction, subscripts s and b designate surface and bulk conditions, respectively, and L represents the total number of gas components being transported to or from the particle. The quantity N_m is negative for components being consumed at the particle surface (oxygen) and positive for components being generated at the particle surface (vapors and products of oxidation).

The mass transfer coefficient is calculated from a Sherwood number (Sh) correlation given by

$$Sh_m \equiv \frac{f_m d_p}{c_t D_{m\text{-mixture}}} = 2.0 + 0.6 Re_p^{1/2} Sc_g^{1/3} \quad (41)$$

where c_t represents the total molar concentration of gases and $D_{m\text{-mixture}}$ represents the effective diffusion coefficient of component m in the mixture of gases surrounding the particle. The Schmidt number, Sc_g , is the ratio of the gas kinematic viscosity to the diffusivity.

Under appropriate simplifying assumptions one can show that the low Reynolds number limit of the Sherwood number is 2 and that the exponents of the Reynolds and Schmidt numbers are 1/2 and 1/3, respectively. The factor 0.6 is a correlating parameter. One of the simplifying assumptions required to obtain these results is that the net rate of mass transfer to the particle is zero. In most cases, this is invalid. The parameter θ_m in Eq. (40) is called the blowing factor and corrects for this assumption.

The blowing factor, as derived from film theory [Bird, Stewart et al. 1960], is defined as follows

$$\theta_m = \frac{\phi_m}{e^{\phi_m} - 1} \quad (42)$$

where

$$\phi_m = \frac{\frac{dm_p}{dt}}{Z^{og} A_p t_m} \quad (43)$$

where m_p is the total particle mass, Z^{og} is the overall molecular weight of the gas, and A_p is the particle external surface area. This blowing factor can be derived by analogy to the blowing factor for heat transfer discussed above.

The surface concentration of oxygen is determined by assuming the particle behaves in a pseudo steady-state manner and burns in a single-film mode. These approximations indicate that the fluxes of oxygen through imaginary spheres of any diameter greater than the particle diameter are equal (single-film mode) and that these fluxes equal the rate of oxygen consumption by chemical reaction at the particle surface (pseudo steady-state). The latter rate is determined from chemical kinetics.

The rate of coal, char, and inorganic heterogeneous reaction is assumed to be given by an Arrhenius expression. A global reactivity is used as the basis for this expression. Two fundamentally different points of departure for global reactivities are used in the literature: one presumes reaction rates are proportional to surface oxygen concentrations [Laurendeau 1978] and the other presumes they are proportional to surface oxygen partial pressures [Mitchell 1987]. The intent of this model is to make use of data of both types. Therefore, the following expression is used to describe the surface reaction rate between oxygen and coal/char:

$$r_1 = \xi k_x T_p^m p_{O_2,s}^n = \xi k_x R_g^n T_p^{m-n} C_{O_2,s}^n \quad (44)$$

The value of the temperature exponent m is 0 for partial-pressure kinetics and $-n$ for concentration kinetics. The parameter ξ is the ratio of active surface area to external surface area and can be used to incorporate intrinsic kinetics in the model.

The concentration of oxygen at the particle surface is determined by equating the rate of oxygen consumption indicated by Eq. (44) with the flux of oxygen indicated by Eq. (40). This yields the following implicit expression for oxygen mole fraction at the particle surface

$$x_{O_2,s} = \frac{x_{O_2,b}}{1 + \frac{\xi \phi k_s T^{m+n} (R_g c_{t,s})^n x_{O_2,s}^{n-1}}{M^c \theta_m h_{O_2}} + \frac{\sum_k N_k}{\theta_m h_{O_2}}} \quad (45)$$

where ϕ represents the ratio of the number of moles of oxygen consumed per mole of reactant, as discussed later. As the rate of chemical reaction increases, the concentration of oxygen at the surface decreases, leading to a limit known as Zone III combustion. In this limit, the concentration of oxygen at the surface is negligible compared to that in the bulk and the total flux of oxygen is accurately given by assuming the surface fraction of oxygen is zero in Eq. (40).

The rate of oxidation is given by multiplying the flux of oxygen to the external surface by the external surface area and the stoichiometric ratio of moles of solid produced per mole of oxygen consumed. Units are converted to mass units by using the oxide molecular weight:

$$r_{ox}^+ = N_{O_2} A_p \frac{\zeta_{os}}{\zeta_{O_2}} Z_{ox} \quad (46)$$

where Z_{ox} is the molecular weight of the oxide, and ζ_m is the stoichiometric coefficient of component m in the chemical equation describing the oxidation reaction

The reactants and products in Eq. (47) are represented by R_m and P_m , respectively. The subscripts M , O_2 , and ox represent condensed-phase material (char, inorganics, etc.), oxygen, and oxidized product, respectively. The available external surface area for the oxidizing species is assumed to be proportional to their volume fractions in the char.

Devolatilization is modeled using available simple models [Ubhayakar, Stickler et al. 1976] that have been shown to be in reasonable agreement with more recent and sophisticated models [Serio, Hamblen et al. 1987; Fletcher 1989; Chen and Niksa 1992; Chen and Niksa 1992]. This simple model is limited to predicting overall particle mass loss. As more detail of the

devolatilization process is required, a more advanced model, such as the CPD model, may be incorporated in the code. The rate of particle mass loss (volatile production) is

$$\frac{dm_v}{dt} = r^v = \sum_{k=1}^2 \alpha_k A_k^v m_c \exp\left(-\frac{E}{R_g T_p}\right) \quad (48)$$

The kinetic parameters for each reaction are α , A^v , and E^v . The rate of char production, r is related to the rate of volatile production

$$\frac{dm_h^+}{dt} = r^{+h} = \sum_{k=1}^2 (1 - \alpha_k) A_k^v m_c \exp\left(-\frac{E}{R_g T_p}\right) \quad (49)$$

The only two products of coal devolatilization are char and volatiles, as can be verified by examining these two equations. The total rate of coal reaction by devolatilization is the sum of r^v and r^{+h} .

The total rate of mass change in the coal particle is given by

$$\frac{dm_p}{dt} = r_p \quad (50)$$

where r_p is the total rate of mass loss from the particle by all mechanisms. Equations describing vaporization, oxidation, and devolatilization are discussed above. Several of the inorganic components undergo additional mass loss by drying or dehydrating (clays), thermal decomposition (pyrite and carbonates), etc. These processes are not yet incorporated in the model.

The total rate of mass change of each component is computed as the sum of the rates of mass loss and mass gain:

$$r_m \equiv \frac{dm_m}{dt} = r_m^+ + r_m^- \quad (51)$$

where the rates of mass addition are attributed to formation of an oxide and the rates of mass depletion are attributed to vaporization, thermal decomposition, and disintegration of fragile structures. The total mass of each component is computed by integrating Eq. (51) and accounting for phase changes. The total mass of the particle is computed by summing the mass of the condensed phase components

$$m_p = \sum_m \xi_m m_m \quad (52)$$

where the summation is over all condensed-phase components. The value of ξ_m is assumed to be unity unless otherwise specified. A value less than unity indicates that the component loses mass by decomposing during reaction, as in the case of unoxidized pyrites. The instantaneous

composition of the particle is determined by dividing each of the component masses by the total particle mass.

These equations form the backbone of the particle description in the model. There are many areas in which the inorganic descriptions lack the detailed physical property descriptions that could be used by the code.

7. Deposition Mechanisms

Coal particles, including ash described in terms of these mineral species, are tracked as a function of particle residence time through the pulverized coal boiler as described above. This model yields particle mass, size, velocity, and composition as a function of particle residence time, or position, in the boiler. Representative particles that differ by their initial size, composition, starting location, velocity, or temperature are tracked through the boiler one by one. Each of these particles represents a fraction of the total mass feedrate of particles to the boiler. As the particles encounter surfaces, a fraction of them deposit on the surface. The discussion below centers on the computation of the fraction of particles that collects on the surface of the boiler at any given residence time (location) in the boiler.

The four deposition processes treated in the model are: (1) inertial impaction (and particle capture), (2) thermophoresis, (3) condensation, and (4) heterogeneous reaction. All heat transfer surfaces are involved in these processes. The model currently uses flat walls in turbulent flows as an approximation to waterwalls and single tubes in cross flow as an approximation to convective pass tubes. The four processes of ash deposition are assumed to have additive influences on deposit composition. That is, the rate of accumulation of ash on the surface of a heat transfer tube is written as

$$\frac{dm_m}{dt} = I_m(\tau, t)G_m(\tau, t) + E_m(\tau) + T_m(\tau, t) + C_m(\tau, t) + R_m(\tau, t) \quad (53)$$

In this equation, m_m represents the mass of component m in the deposit. The factor I_m represents the rate of inertial impaction, E_m represents the eddy impaction rate, G_m represents the relative particle capture efficiency, T_m represents the rate of thermophoretic deposition, C_m represents the rate of condensation, and R_m represents the rate of chemical reaction. The subscript m refers to each of the species discussed previously. Before describing each of these terms in more detail, some explanation of the two independent variables is in order.

Two time scales are identified in Equation (53). The variable t is a material time scale, designating particle residence time relative to the time of injection of the particles. The variable τ designates elapsed or laboratory time, i.e., time relative to an arbitrary time of day independent of the particle residence time. In a steady-state or stationary system, the only relevant time scale is t . Ash deposition rates, composition, and all other characteristics of the process would have the same mean values at all times at a given location. However, ash deposition clearly is a non-stationary process [Baxter, Hencken et al. 1990; Beér, Monroe et al. 1990]. Therefore, both the material and elapsed time scales must be addressed. Equation (53) can be thought of as an ordinary differential equation parameterized by the variable τ .

Practical illustrations can be used to clarify the differences in the two time scales. Changes in deposit composition from one location to another in a boiler are indicative of variation of one or more of the terms in Eq. (53) with particle residence time (t). For example, our experience,

consistent with industrial observations, is that ash deposits formed from eastern, pyrite-bearing coals are enriched in iron. This enrichment is most pronounced when the deposits are sampled near the burners, with typical enrichments of 60 %. Deposits sampled midway between the burners and the furnace exit are slightly less enriched in iron. A typical enrichment of 40 % may be observed in this area. Near the furnace exit, iron enrichment in the deposit drops to 10 - 20 %. This change in deposit composition with location in a boiler is a reflection of the residence time (t) dependence of the inertial impaction and particle capture efficiency terms in Eq. (53).

Changes in deposit composition as a function of deposit thickness are indicative of variation of one of the terms in Eq. (53) with clock time (τ). With respect to our previous example, industrial experience suggests that wall deposit composition in the radiant section of a boiler is not strongly dependent on deposit depth unless there is a change in boiler operating parameters [Borio and Levasseur 1991]. That is, the deposit usually has about the same composition at the outer edge as on the inner surface next to the heat exchanger surface. Therefore, the dependence of the inertial impaction term on τ would be expected to be minimal in this section of the boiler. By contrast, the deposits formed in the convection pass of boilers firing both eastern and western coals typically show pronounced variation in composition between the heat exchanger surface and the outside of the deposit. These composition changes are related to the variation of terms in Eq. (53) with τ .

The six functions in Eq. (53), I , E , G , T , C , and R are discussed in more detail below. The first third and fourth terms are developed in some detail first, since they denote the processes that dominate ash deposition in the furnace region of a boiler during the combustion of bituminous coals. The remaining terms are discussed more briefly.

Inertial Impaction I (t , τ)

Inertial impaction is generally the process by which the bulk of the ash deposit is transported to the heat transfer surface. Particles depositing on a surface by inertial impaction have sufficient inertia to traverse the gas stream lines and impact on the surface. The particle capture efficiency describes the propensity of these particles to stay on the surface once they impact. Both particle and surface properties play significant roles in determining the particle capture efficiency.

The controlling issue for inertial impaction is the relative magnitudes of the particle and fluid relaxation time or length scales. Specifically, inertial impaction occurs when the distance a particle travels before it fully adjusts to changes in the fluid velocity is larger than the length scale of an object, or target, submerged in the fluid. The particle Stokes number is defined as the ratio of these length scales. It is reasonable to expect, then, that particle impaction efficiencies can be correlated with suitably defined Stokes numbers for a wide range of particle and fluid properties. In this section we examine the success of such correlations by comparing their predictions with fundamentally determined impaction efficiencies for realistic flows.

The total mass flux of particles is computed as a function of particle residence time from the product of the deposition fluxes and the total surface area available for deposition.

$$q_m(t + dt) = A_t \frac{dm_m}{d\tau} q_m(t) \quad (54)$$

The rate of inertial impaction is the product of the total mass flux of particles in the flow and the fraction of these particles — which we call the impaction efficiency — that actually strike the surface. That is,

$$I_m(Stk) = q_m \eta_m \quad (55)$$

where q_m is the local particle flux, Stk is the Stokes number, and η_m is the impaction efficiency. The point of evaluation of q_m , and Stk and the functional form of η_m differ for cylinders and walls. The details of these differences and correlating expressions for η_m are discussed below.

Cylinders in Cross Flow. Inertial impaction is schematically illustrated in Figure 46 for the case of a cylinder in cross flow. Two particles are illustrated as they approach the cylinder. Both respond to the gas flow field around the cylinder by beginning to move around the cylinder on approach. However, in both cases, the particle inertia overwhelms the speed with which the particle responds to the gas flow, and both particles impact on the cylinder. One is shown rebounding and the other sticking to the surface. Gas stream lines, including recirculation zones, are shown in light gray in this and subsequent similar figures.

Figure 46 Conceptual illustration of inertial impaction mechanism on a cylinder in cross flow. The deposit is typically confined to the leading edge $\pm 50^\circ$ of the cylinder. Two particles are also illustrated, one which rebounds and one which sticks.

This process is most important for large particles (10-15 μm or larger) and results in a coarse-grained surface, as illustrated. The rates of impaction are highest at the stagnation point on the cylinder, decreasing rather rapidly with angular position along the surface as measured from this stagnation point. At angular displacements larger than about 50° , the rate of inertial impaction drops to essentially zero under conditions typical of boiler operation. Thus, the deposits formed from inertial impaction mechanisms are often bell-shaped, as is also illustrated. (Further discussion of this aspect of inertial impaction is included below in an illustration of the application of the model.)

Mathematically, the rate of impaction is described in the reference frame illustrated in Figure 47.

Figure 47 Schematic diagram of coordinate system and reference frames used in describing a tube in cross flow.

A cylinder is shown in cross section in a parallel, constant velocity flow field. Gas velocity components will be expressed in both Cartesian and cylindrical coordinates and given the variable name u with specific subscripts to avoid confusion with the indicial notation used previously. Potential flow theory is used to describe the flow of gas around the cylinder. According to this theory, the x and y components of velocity around the cylinder are given by [Bird, Stewart et al. 1960]

$$u_x = u^\infty \left[1 - \left(\frac{R}{r} \right)^2 \cos(2\theta) \right] \quad (56)$$

and

$$u_y = u^\infty \left(\frac{R}{r} \right)^2 \sin(2\theta) \quad (57)$$

or, in terms of cylindrical coordinates,

$$u_r = u^\infty \left[1 - \left(\frac{R}{r} \right)^2 \right] \cos(\theta) \quad (58)$$

and

$$u_\theta = -u^\infty \left[1 + \left(\frac{R}{r} \right)^2 \right] \sin(\theta) \quad (59)$$

where u^∞ is the gas free stream velocity (assumed to be aligned with the x coordinate direction), R is the cylinder radius, and r is the radial distance to the point for which the velocity components are being calculated. Equations (56) through (59) are assumed to be correct everywhere in the flow field except within the boundary layer. Within the boundary layer, the velocity components are interpolated from tabulated results [Schlichting 1979].

Particles are introduced to this flow field far upstream and their positions are predicted according to the particle equation of motion (Eq. (16)). As an illustration of the calculations, average particle streak lines are shown in Figure 48 upstream of the cylinder. The particles respond to the flow field stream lines around the cylinder; depending upon the particle size, density and velocity and the size of the cylinder, some fraction of the particles impact the tube. An impaction efficiency (η) for a uniform flow of identical particles can be defined, as illustrated in the figure, in terms of the cylinder diameter and the distance between the outermost particle streak lines that reach the cylinder surface.

Figure 48 Illustration of particle steak lines and definition of particle impaction efficiency for a cylinder in cross flow.

Theoretical predictions of the impaction efficiency as a function of particle, gas, and tube properties have been published, for various levels of approximation, by numerous investigators

[Israel and Rosner 1983; Loehden, Walsh et al. 1989; Walsh, Sayre et al. 1990; Walsh, Sarofim et al. 1992]. In particular, we are interested in: (1) the importance of including the viscous boundary layer in performing the predictions; (2) the relative importance of thermophoresis at the large particle sizes; (3) resolving the rate of deposition as a function of position along the cylinder surface, and; (4) evaluating the importance of turbulent fluctuations of gas velocity on the impaction efficiency. Typical results are illustrated in Figure 49.

Figure 49 Theoretical calculation of particle impaction efficiencies as a function of particle size at three levels of sophistication.

Boundary Layer (and Thermophoretic) Effects. The impact of the fluid dynamic boundary layer around the cylinder was investigated. Predicted impaction efficiencies are illustrated at three increasingly sophisticated levels of solution. The first solution uses only the potential flow description of the flow field (Eqs. (56) to (59)). In this approximation, the fluid velocity (unrealistically) maximizes at the surface of the cylinder, becoming twice the free stream velocity at an angle of 90° . The second level of approximation includes the effect of the boundary layer and the third includes the effects of both the boundary layer and thermophoresis. (Modeling of thermophoresis is discussed later.) The data presented in the figure are in essential agreement with classical predictions [Brun, Lerous et al. 1955] and correlated by [Israel and Rosner 1983] over most of the particle size range.

It is clear from these predictions that, at most particle sizes, the boundary layer has essentially no effect on the particle impactation efficiency. This is the most important conclusion from Figure 49. However, the details of the figure indicate that at small particle sizes the boundary layer can either slightly enhance or significantly retard particle impactation. For example, the impactation efficiency for particles less than $15\ \mu\text{m}$ in diameter is predicted to be many times higher (although near zero), using potential flow only, than when using the more complete solution including the effects of the boundary layer. This predicted retardation of inertial impactation results from the boundary layer stopping the particles before they reach the surface. At slightly larger particle sizes ($\approx 20\ \mu\text{m}$) the rate of impactation is enhanced rather than retarded. At these sizes, the boundary layer has the effect of increasing the particle residence time near the cylinder surface by decreasing its tangential velocity component. This increased residence time allows up to 20 % more of the particles to impact on the surface than is predicted in the absence of the boundary layer.

Angular Dependence of Impactation Efficiency. Figure 50 illustrates predicted impactation efficiencies (expressed as a percent) per degree arc length as a function of angle along the surface for $50\ \mu\text{m}$ diameter particles under the conditions indicated in Figure 49.

Figure 50 Predicted particle impactation efficiency (expressed as a percent) as a function of angular position measured from the leading edge of a cylinder in cross flow.

The practical interpretation of these data relates to the initial shape of the deposit that grows on a surface, assuming particle capture efficiencies are independent of angle of approach, velocity, time, or position on the tube. (Capture efficiencies are discussed later). Each curve in the figure indicates the predicted height of the deposit as a function of angular position. Four curves are presented in which the total rate of deposition is used to normalize the data. Two of these curves are representative of the deposit height as a function of angular position as measured radially from the surface. These are labeled total surface area. Two additional curves are presented that represent the height of the deposit as measured in the direction of the oncoming flow. This is equivalent to measuring the deposit height in the direction of the flow. In each case, both the potential flow and complete solutions are indicated. Note that the abscissa is labeled in terms of the angle as measured from the forward stagnation point, or 180° minus the angle as defined in Figure 47.

The ordinate is the rate of impaction per degree arc, normalized by the particle flux. The figure indicates that approximately 1.75 % of the total particle mass approaching the tube impacts within one degree of arc on the tube leading edge. This fraction decreases, slowly for the first 15° then more rapidly for points beyond approximately 20° from the forward stagnation point. Essentially no mass is collected at angles larger than 55° from the forward stagnation point.

As particle velocity or density decreases, or as tube diameter increases, the fraction of material impacting at all angles other than zero decreases and the curves shown in Figure 50 become increasingly narrow. A similar trend is seen with decreasing particle size until the particles become sufficiently small that thermophoresis is the dominant deposition mechanism. At this point, the curve begins to broaden, indicating that the deposit thickness becomes more uniform around the tube.

Experimental observations at Sandia and elsewhere indicate that deposits formed from bituminous coals often take on the shape suggested by Figure 50. On the other hand, some deposits, especially those from low-rank coals, grow rapidly at angular displacements of 30 – 45° [Benson, Steadman et al. 1990]. There is no simple aerodynamic explanation for these results. However, one explanation is that the deposits collected at angles greater than 35° would be expected to be dominated by thermophoretic or condensed material. Therefore, the tube surface at these locations would be of different composition and expected to have a different capture efficiency than at smaller angles. Note also that the deposit shape illustrated in (45) is valid only for the initial inertial impaction deposit. As the flow field adjusts to the growing deposit, the flow field description in Eqs. (56)–(59) is no longer valid.

Effect of Turbulence. The predictions illustrated thus far have assumed that all particles experience the average gas velocity, consistent with the bulk of the literature. The impact of turbulent fluctuations in the oncoming particle velocity can be accounted for analytically as follows

$$\eta^*(d_p) = \int_{-\infty}^{\infty} \eta(u_p; d_p) P(u_p; d_p) du_p \quad (60)$$

where $\eta^t(d_p)$ is the particle impaction efficiency accounting for turbulent fluctuations as a function of particle diameter, P is the probability density function for particle velocity, and the remaining terms have already been defined.

The predicted variation of η with particle Stokes number assuming several levels of turbulent intensity is illustrated in Figure 51 for the case of a cylinder in cross flow. In these simulations, the Stokes number, Stk^c , is defined as follows:

$$Stk^c \equiv \frac{\rho_p d_p^2 \langle u_p \rangle}{9\mu_g d_c} \Psi \quad (61)$$

where $\langle u_p \rangle$ is the ensemble average particle (and gas) velocity in the bulk flow and Ψ is a correction factor for non-Stokesian drag effects [Israel and Rosner 1983], which is near unity in most cases of practical interest in pulverized coal combustion. The remaining terms were previously defined. The gas viscosity, μ_g , is evaluated at the temperature of the bulk gas stream. The superscript c on the Stokes number indicates it relates to tubes in cross flow.

Figure 51 Sensitivity of particle impaction efficiency to turbulent fluctuations in the gas and particle velocity. A Gaussian distribution of velocity fluctuations was assumed in making these predictions.

As can be seen, the effect is very slight. Gaussian distributions in gas and particle velocity were assumed in performing these calculations. Few flows experience turbulent intensities as large as 0.3 (0.1 is a typical upper bound), therefore the plot covers both the Stokes number and turbulence intensity ranges of interest to pulverized coal combustion. If the turbulent velocity distribution is not symmetric, the effect of turbulence on the predicted impaction efficiency is only slightly more pronounced, as is shown in Figure 52, where the velocity fluctuations are assumed to be described by a Rayleigh distribution, given by

$$f(x, \alpha) = \begin{cases} 2\alpha x \exp(-\alpha x^2) & 0 < x < \infty \\ 0 & x \leq 0 \end{cases} \quad (62)$$

These results do not imply that η is insensitive to gas or particle velocity. Rather, the mild sensitivity of the impaction efficiency to turbulence reflects increased impaction efficiencies resulting from positive fluctuations being offset by decreased impaction efficiencies associated with negative fluctuations.

Figure 52 Sensitivity of particle impaction efficiency on a tube in cross flow to turbulent fluctuations in gas and particle velocity. A (skewed) Rayleigh distribution of velocities was assumed in making these predictions.

Correlating Expression. The previous discussion demonstrates the general insensitivity of the impaction efficiency to near-surface phenomena and turbulent fluctuations. The results of the predictions with the fundamental model, derived from Eqs. (56)-(59), are compared with the literature correlation [Israel and Rosner 1983] in Figure 53. Note that the Stokes number is evaluated using the properties of the free stream (as could be anticipated considering the relative unimportance of the boundary layer on the predictions). The agreement is satisfactory for the purposes of our engineering model. The slight disagreement at small Stokes numbers is consistent with the low Reynolds number results illustrated by the previous investigators [Israel and Rosner 1983]. A slightly better agreement at low Stokes numbers was obtained by fitting the coefficients in the expression to our calculations. Two fits are illustrated. The first, designated 'a', corresponds to the solution including thermophoresis and the second, designated 'b', corresponds to the solution neglecting thermophoresis. The overall impaction efficiency on a cylinder in cross flow is given by the function $R(Stk)$ as follows:

$$\eta_m(Stk^c) \equiv \left[1 + b(Stk^c - a)^{-1} - c(Stk^c - a)^{-2} + d(Stk^c - a)^{-3} \right]^{-1} \equiv R(Stk^c) \quad (63)$$

where a , b , c , and d are the correlating parameters. The values of the parameters are given in for the three correlations illustrated in Figure 43. For values of Stk^c less than 0.14, none of the functions is accurate.

Figure 53 Correlation of particle impaction efficiency as a function of Stokes number. Points are from our calculations. Original function is from the literature [Israel and Rosner 1983]. Modified (and original) function parameters are presented in Table 11.

The term I_m is calculated from the impaction efficiency to yield a particle impaction flux as follows:

$$I_m(Stk^c) = q_m \eta_m \quad (64)$$

where q_i is the mass flux (kg/cm²-s) of particles of type m with Stokes number Stk^c in the (undisturbed) flow approaching the cylinder. The residence time dependence is introduced through time-dependent particle sizes, particle flow rates, etc. A complete description of impaction would include the τ dependence of the impaction efficiency deriving from changes in the shape of the cylinder as the deposit grows.

Table 11 Original and Modified Coefficients in the Correlating Expression for Particle Impaction Efficiency on Cylinders in Cross Flow

	a	b	c	d
Original	0.125	1.25	-0.014	0.00508
Modified - a	0.1425	1.28	0.00215	0.00587
Modified - b	0.1238	1.34	-0.034	0.0289

Flat Plates. Two fluid-dynamic features that were shown to have very little influence on the predicted rate of inertial impaction for cylinders in cross flow were the laminar boundary layer and the turbulent fluctuations. These results should not be hastily generalized to other geometries. The same two fluid dynamic features have a dominant influence on the rate of inertial impaction on flat plates in parallel flow; indeed, they become the central parameters in the definition of the Stokes number in this geometry.

Correlating Parameter and Conceptual Definitions. The definition of the particle Stokes number with respect to a wall or flat plate can be approximated as follows:

$$Stk^w = \frac{\rho_p d_p^2 [\hat{u}_p + \sigma_{u_p}]}{9 \mu_g \delta_w} \psi \quad (65)$$

where $\hat{u}_p$ and σ_{u_p} represent the *median* and standard deviation of the particle velocity component normal to the wall at the edge of the boundary layer. This allows for flows impinging on a wall as well as parallel flows. As shown later, use of the median velocity rather than the mean results in a more accurate correlation of the impaction efficiency. The median value is the value above and below which there is a 50 % probability of finding the instantaneous value. This is equivalent to the average (or expected) value only for symmetrical velocity probability distributions. The target dimension (δ_w) is the boundary layer thickness. The gas viscosity in this case is evaluated at the mean of the wall and free stream temperatures. The median particle velocity at the edge of the boundary layer is non-zero in cases of flows with mean components directed toward the wall and skewed velocity distributions.

The impactation efficiency for a flat plate indicates the fraction of particles at the edge of the boundary layer that will ultimately impact on the wall. The equation of motion for a particle entering a fully developed boundary layer indicates that the initial particle velocity must exceed a critical value for the particle to reach the wall. The Stokes number, defined in Eq. (65) for a wall, is the ratio of the distance the particle travels by inertia (the stopping distance) to the thickness of the boundary layer. The success of the wall Stokes number Stk_p^w as a correlating parameter for impactation efficiencies is still under investigation. It will be illustrated, however, that the impactation efficiency depends not only on the magnitude of the fluctuations, but also on the shape of the distribution.

Effect of Turbulence. Figure 54 illustrates the impactation efficiency as a function of particle Stokes number for a flat plate, assuming Gaussian and Rayleigh probability density functions (pdfs). The predicted impactation efficiency based on the median velocity alone would be zero (for a Gaussian profile) for all particles. This contrasts strongly with the results for the cylinder in cross flow. Whereas the fluid dynamic boundary layer around a cylinder in cross flow plays only a minor role in determining rates of inertial impactation, the boundary layer along a wall is the dominant fluid dynamic feature. Although turbulence levels have little impact on particle impactation rates as a function of particle Stokes numbers for cylinders, in many applications the turbulent fluctuations can be the only mechanism for inertial impactation on a flat wall in fully developed turbulent flow.

Figure 54 The predicted impactation efficiency of particles on flat plates as a function of particle Stokes number.

The two lines for the Rayleigh pdfs illustrate the sensitivity of the parameter to the shape of the pdf. The two lines are based on the same functional form. Only the direction of skewness was changed. There is clearly a greater amount of disparity between these predictions and those previously presented for a cylinder in cross flow. The region of the figure in which there is the greatest disparity among the several predictions, i.e., $Stk^w \leq 4$, is relevant to a large fraction of a typical particle flow stream. Therefore, there is significant uncertainty in the prediction of the impaction efficiency for flat plates.

Correlating Expression. The complementary error function correlating expression illustrated in Figure 54 (indistinguishable from the Gaussian results) is theoretically derivable based on assumed Gaussian pdfs for particle velocity. This correlation is currently used in the same manner that the function R is used to correlate impaction rates on cylinders in cross flow (see Eq. (64)). Specifically,

$$\eta_m(Stk^w) \equiv 0.5 \operatorname{erfc}\left(\frac{Stk^w}{\sqrt{2}}\right) \quad (66)$$

This impaction efficiency is combined with the flux of particles along the wall of the boiler in the same manner as is shown in Eq. (64) to predict the mass flux of each species by inertial impaction.

It is important that the proper definition (that is, the one given by Eq. (65)) of the Stokes number be used in making these predictions. Using the mean velocity instead of the median leads to less satisfactory results, as shown in Figure 55. These predictions are identical to those shown in Figure 54, except that the Stokes number is calculated using the mean velocity. Also shown is the correlation for the cylinder (divided by two) for comparison to the flat plate.

In summary, rates of inertial impaction on both flat plates and cylinders can be predicted from fundamental descriptions of fluid and particle mechanics. These descriptions are for idealized flows, ignoring features such as developing boundary layers, transient fluid mechanics, wake effects, and changes in target geometry with time. However, they provide reasonable estimates of first-order effects associated with particle velocity, diameter, and density and fluid mechanics in the vicinity of the deposition surfaces. Correlations have been shown that allow more efficient computation of the impaction rates.

Capture Efficiency $G(t, \tau)$

The particle capture efficiency term (G) in Eq. (53) is essentially empirical, in contrast to the inertial impaction term. This term is defined as the ratio of the number of particles adhering to or captured by the target surface to the number of particles impacting on the surface. The term G_m indicates a relative capture efficiency whereas γ_m (used in previous reports and publications [Baxter and Hardesty 1990]) indicates an absolute capture efficiency. The former can be greater or less than one and is only important relative to the values of the other G_m 's.

Figure 55 Illustration of the impact of using the velocity mean rather than median in the Stokes number calculation for flat plates. Also shown for comparison are the correlations for the cylinder in cross flow (divided by 2) and for the flat plate.

The latter is needed to predict rates of deposition and has been demonstrated to have large time (τ) variations [Baxter, Hencken et al. 1990]. The relative value is essentially independent of τ in conditions representative of the radiant section of the boiler, as indicated by essentially no variation in deposit composition with depth of deposit. Knowledge of γ_m for even one of the species will allow calculation of the absolute values from the relative values and, therefore, calculation of the rate of ash deposition in addition to its composition. We have incorporated these absolute capture efficiencies but have not evaluated their accuracy.

In practical systems, where surface properties are changing, the variation of γ with surface properties must also be addressed in addition to the variation with particle properties. That is, both soft particles impacting hard surfaces and hard particles impacting soft surfaces experience high capture efficiencies. Surface viscosity and morphology influence collection efficiency. Powdery surfaces can be as effective in capturing particles as 'sticky' surfaces.

Our current approach correlates empirically the capture efficiencies as a function of particle residence time in a boiler and as a function of time with respect to the last surface cleaning. The correlating function with respect to particle residence time is based on the following two assumptions: (1) the capture efficiency of a given ash species should approach some constant value in the limit of long residence times; and (2) the rate at which the capture efficiency approaches this limiting value is proportional to its difference from the value. These

assumptions describe a first-order, linear variation of the capture efficiency with time that can be described by the following differential equation:

$$\frac{dG_m}{dt} = \alpha_m (G_m^\infty - G_m) \quad (67)$$

subject to the initial condition

$$G_m(t = 0) = G_m^0 \quad (68)$$

where G_m is the particle capture efficiency, G_m^∞ , is the ultimate value, α is the proportionality constant that determines the rate at which the capture efficiency approaches its ultimate value, and G_m^0 is its initial value. The algebraic solution to Eqs. (67) and (68) (assuming constant α) is given by

$$G_m(t, \tau) = G_m^\infty(\tau) - (G_m^\infty(\tau) - G_m^0(\tau)) \exp(-\alpha t) \quad (69)$$

These values and a typical variation of the capture efficiency with particle residence time are illustrated in Figure 56. Particle residence time has been normalized with α in this figure. The three parameters α , G^∞ , and G^0 are determined empirically for each of the species in the fuel, but independent of coal rank, based on deposit composition data collected in the MFC. These empirical correlations combined with the more fundamental impaction data combine to form the first term of Eq. (69).

Figure 56 Illustration of the parameters and form of the correlating expression used to describe particle capture efficiencies for both tubes in cross flow and flat plates.

Thermophoresis $T(t, \tau)$

Thermophoresis is the process of particle transport in a gas due to local temperature gradients. Thermophoretic forces on a particle may be induced either by the temperature gradient in the gas (in which the particle is suspended) or as a consequence of a temperature gradient in the particle itself. In general, these forces act in the direction opposite to that of the temperature gradient, although they can act in the direction of the gradient under certain conditions of particle surface temperature.

An illustration of thermophoretic deposition is presented as Figure 57. Thermophoretic deposits are finer grained and more evenly distributed around the tube surface than deposits formed by inertial impaction, as indicated. As deposits accumulate on the tube surface, the temperature gradient in the thermal boundary layer decreases, decreasing the rate of thermophoresis.

Figure 57 Schematic illustration of thermophoretic deposition on a tube in cross flow.

Mechanistic Descriptions. There are at least two mechanisms that give rise to this force. The first mechanism is that of the high-temperature gas molecules colliding with one side of the particle with more energy and at a higher collision frequency than the low-temperature molecules on the opposing side of the particle. This creates a greater pressure on the high temperature side of the particle than on the opposing side, resulting in a force opposite the direction of the temperature gradient. For the case of an isothermal particle, this force is proportional to the particle cross sectional area and the gradient in gas temperature and is given by [Cawood 1936; Einstein 1954]:

$$F_T = -\frac{\pi p \lambda d_p^2}{8 T_g} \nabla T_g \quad (70)$$

Mechanistic Descriptions. There are at least two mechanisms that give rise to this force. The where F_T is the thermophoretic force, p is the total pressure, λ is the mean free path of the gas, and T_g is the gas temperature. Note that the force is independent of both total pressure (the product of $p \lambda$ is independent of pressure) and gas thermal conductivity. The assumption that the particle is isothermal is equivalent to assuming that the particle thermal conductivity is large compared to that of the gas. This equation is valid for $d_p \ll \lambda$.

As particle size increases beyond the mean free path of the gas molecules, the particle temperature gradient must be considered, giving rise to a second, and often dominant, mechanism of thermophoresis. This mechanism can be described in terms of a particle with an internal temperature gradient suspended in an arbitrary gas. At the particle surface, the particle and the gas temperatures are considered equal as a function of angular position around the particle and momentum balances are performed between the two phases. The molecules approaching the surface from the direction of the hot gases have, again, both greater average momenta and more rapid average collision rates than those approaching from the direction of the cold gases. This induces a net force on the particle in the direction of the cold gases. The gases experience an equal but opposite force, establishing a convection in the direction of the hot gases. (Note that the convection of gases in this radiometric flow is in the opposite direction as the force on the particle, as opposed to viscous flow, where they are in the same direction). The force induced on the particle is given by [Hettner 1926]:

$$F_T = -\frac{3\pi R_g \mu_g^2 d_p}{2pM} \nabla T_p \quad (71)$$

where R_g is the gas constant and M is the molecular mass of the gas. Note that the gradient is now with respect to particle temperature rather than gas temperature.

A particle temperature gradient can be caused by reaction rates, radiative and convective heat transfer, or a gas temperature gradient. In some cases, where the particle temperature gradient is established by radiative interactions with hot walls (photophoresis), the particle and gas temperature gradients can have opposite signs [Castillo, W.Mackowski et al. 1990]. For the purposes of our discussion, the particle temperature gradient will be assumed to be entirely due to a gas temperature gradient, in which case the thermophoretic force has been expressed as [Fuchs 1964]

$$F_T = -\frac{9\pi k_g \mu_g^2 d_p}{2\rho_g T_g (2k_g + k_p)} \nabla T_g \quad (72)$$

where k_i is the thermal conductivity of the gas ($i=g$) or particle ($i=p$) and the remaining terms were defined previously.

Note the different trends in this expression for the thermophoretic force and that of Eq. (70). Equation (72) indicates a linear dependence on particle diameter, an inverse dependence on gas

pressure (through the term ρ_g), and a slightly less than linear dependence on gas thermal conductivity (the sum in the denominator is typically dominated by k_p). Furthermore, the force predicted in by Eq. (70) vanishes as k_p approaches infinity.

The ratio of the mean free path to the particle radius ($2\lambda/d_p$) is defined as the Knudsen number and indicates the applicability of Eq. (70) vs. Eq. (72). In flows of practical interest ($p = 1$ atm, $T_g = 1700$ K, molecular diameter $= 3 \times 10^{-10}$ m), the gas mean free path is approximately $0.6 \mu\text{m}$. This yields a particle Knudsen numbers of 6 for a $0.1 \mu\text{m}$ particle and 0.6 for a $1 \mu\text{m}$ particle. Therefore, the Knudsen number range of interest in this application is in the transition region from free molecular flow to viscous flow, and neither equation is expected to describe thermophoresis over the entire regime.

Expression Currently Employed. There have been many suggested functional forms for the coefficient of the gradient in Eq. (70), most of which involve modification of the dependencies on gas and particle thermal conductivity. A technical review of these functional forms was completed as part of this research project. The coefficient is expected to depend on details of the particle properties such as phase, heat transfer at the surface, etc. We have adopted one functional form and use it generally, since the parameters are not well established for other types of particles. It is based on an integration of particle-gas momentum exchange over the surface of the particle [Jacobsen and Brock 1965] and has been used by other investigators with some success [Im and Chung 1983]. The thermophoretic force in this approach is given by

$$F_T = -6\pi\mu_g d_p f(Kn) \nabla T_g \quad (73)$$

Where

$$f(Kn) = \frac{d_p C_{tm} Kn \left[\left(\frac{k_g}{k_p} + C_t Kn \right) \left(1 + \frac{4a_3 C_m Kn}{3} \right) - \frac{4a_3 C_m Kn}{3} \right]}{2(1 + 3C_m Kn) \left(1 + 2\frac{k_g}{k_p} + 2C_t Kn \right)} \quad (74)$$

where the constants C_{tm} , C_t , C_m , and a_3 are equal to 0.461 m/(sK) , 3.32 , 1.19 , and 2 , respectively. (These constants are associated with thermal velocity, temperature jump, viscous slip, and second order slip, respectively.)

Incorporation in the model. The thermophoretic force is used in the particle force balance to predict trajectories as particles traverse thermal boundary layers. Specifically,

$$\frac{d(m_p u_{i,p})}{dt} = \sum_j F_j = m_p \beta (u_{i,g} - u_{i,p}) + F_T \quad (75)$$

where F_i are the forces on the particles. Equation (75) is solved for the smallest particles ($< 15 \mu\text{m}$) from the edge of the boundary layer to the target surface. (Deposition of larger particles is dominated by inertial impaction, which is described by use of correlated efficiencies without having to do the detailed tracking through a boundary layer.)

Figure 58 Predicted thermophoretic force as a function of particle size using several different models.

The dependence of Eq. (73) on particle diameter is illustrated in Figure 58 and compared to the results from Eqs. (70) (small particles) and (72) (large particles). The same data are illustrated as a function of Knudsen number in Figure 59. Equation (73) shows qualitative agreement at best with Eqs. (72) and (71) at the extremes of small and large particles. The differences in the predicted forces exceed an order of magnitude over most of the relevant range of particle sizes. All of the equations have been “verified by experiment,” as have several other formulations for the thermophoretic force [Friedlander and Johnstone 1957; Byers and Calvert 1969; Friedlander 1977]. However, our literature review suggests that Eq. (73) is as accurate approximation as any, with the possibility of significant variations in the thermophoretic force being traceable to differences in particle properties. Also, the very low forces illustrated in Figure 58 and Figure 59 result from using a model that neglects important aspects of the problem. Fortunately, in our applications, thermophoresis rarely has a major impact on deposition rate or deposit properties

even when the most rapid rates are assumed. The primary influence is on the initial layers (short τ), when the temperature gradients are steepest.

The dependence of thermophoretic force on particle diameter is much greater than the dependence of thermophoretic velocity (i.e., the velocity with which a particle approaches the surface). Because the resistance of the gas phase to particle motion has a nearly identical dependence on size as does the thermophoretic force, the velocity dependence on size is much less pronounced.

Figure 59 Predicted thermophoretic force as a function of Knudsen number over the range of particle sizes of importance in pulverized coal combustion.

Condensation C (t, τ)

Condensation is the mechanism by which vapors are collected on cooled heat transfer surfaces. All vapors that enter the thermal boundary layer around a heat transfer surface and subsequently are deposited on the surface are treated within the condensation term of the model. At least three mechanisms for this process are available: (1) vapors may traverse the boundary layer and heterogeneously condense on the heat transfer surface; (2) vapors may homogeneously nucleate to form a fume and subsequently deposit by thermophoresis on the surface; and (3) vapors may heterogeneously condense on other particles in the boundary layer and arrive at the heat transfer surface by thermophoresis.

An illustration of deposition by condensation on a tube in cross flow is presented in Figure 60. Condensation deposits have no granularity and are more uniformly deposited on the tube than either thermophoretically or inertially deposited material. The deposits are tacky and would be expected to have a major impact on the surface capture efficiency.

The precise role of condensation in deposit formation is not well established. Those who have addressed the issues involved with coupled condensation and thermophoresis show that the observed rates of deposition can vary by about a factor of four depending on assumptions

Figure 60 Schematic illustration of deposition by condensation on a tube in cross flow.

regarding thermodynamics, heterogeneous condensation on particles, and particle loading [Castillo and Rosner 1988; Castillo, W.Mackowski et al. 1990]. Recent experiments in the MFC using low rank coals demonstrate the commonly observed formation of deposits rich in calcium, sodium, and magnesium in regions of heat transfer surfaces that are not affected strongly by inertial impaction. Possible mechanisms for the formation of these deposits include: (1) thermophoretically deposited fume material from the bulk gas phase, (2) condensation of vapors within the thermal boundary layer and subsequent thermophoretic deposition of these particles, or (3) heterogeneous condensation of vapors on the heat transfer surface. All of these mechanisms are likely contributors to the process. Our current hypothesis is that the third is more significant than has been commonly recognized.

Our current approach to modeling condensation is to treat the problem in the frozen boundary layer limit, implying no homogeneous condensation and no scavenging of vapors by small particles in the boundary layer. This is an upper limit for the condensation rate. Since thermophoretic velocities and diffusion rates are slower than the corresponding molecular rates, introduction of either nucleation of vapors or scavenging of vapors by pre-existing particles in the boundary layer decreases the total vapor deposition rate. This upper limit will be augmented by an empirically determined "condensation efficiency" parameter to account for the observed rates of condensation on the heat transfer surface. The value of the empirically determined parameter should lie between about 0.25 and 1.0 and will depend on the ratio of surface and gas temperatures but (presumably) not on coal type. Therefore, the condensation flux is modeled as

$$C_m = \zeta_m \theta (x_{m,b} - x_{m,s}) + x_{m,b} \sum_i C_i \quad (76)$$

Where ζ_m is the condensation efficiency, θ is a blowing factor (which will be very near unity for this application), k_t is a mass transfer coefficient with a value that depends in known ways on geometry, Reynolds number, and fluid properties, and x represents a mole fraction of species m in the bulk gas (subscript b) and at the tube surface (subscript s). The second term on the right side of the equation represents convective transport to the surface and is usually insignificant compared to the first term. The effect of thermophoresis on condensation rate is discussed in the literature [Castillo and Rosner 1988; Castillo, W. Mackowski et al. 1990].

Reaction R (t, τ)

Inertial impaction and thermophoresis describe the two most significant mechanisms for transporting particulate material to a surface. Condensation involves transportation of vapors to a surface by means of a physical reaction and phase change. Chemical reactions, shown schematically in Figure 61, complete the mechanisms by which mass can be accumulated in a deposit. These involve the heterogeneous reaction of gases with materials in the deposit or, less commonly, with the deposition surface itself. The rate of conversion depends on mass transfer rates to the surface and on chemical kinetics of the heterogeneous reactions involved. Many of these reaction rates and their dependence on temperature, gas composition, and deposit morphology and composition are not well characterized. Some of the chemical species found in deposits are not stable at gas temperatures, alkali sulfates being typical examples. The sole source of these species is heterogeneous reactions between gas phase constituents and constituents of the lower temperature deposits. We have not yet incorporated many aspects of the reaction rates within the deposit into the deposition model.

Among the most important chemical reactions with respect to ash deposition are (1) sulfation, (2) alkali absorption, and (3) oxidation. The principal sulfating species of concern are compounds containing the alkali metals, sodium and potassium. Sodium and potassium in the forms of condensed hydroxides and possibly chlorides are susceptible to sulfation.

Silica absorbs alkali material to form silicates. Silicates are less rigid and melt at lower temperatures than silica. The transformations of silica to silicates in deposits can induce

sintering and significant changes in deposit properties. These reactions are relatively slow compared to sulfation.

Residual char often deposits with the inorganic material on combustor surfaces. However, the char oxidizes with locally available oxygen to produce deposits with very little residual carbon. In coal combustion, carbon typically accounts for less than 2 % of the overall deposit mass.

Chemical reactions, such as sulfation of alkali species and combustion of residual carbon in the ash, are similar to condensation in their mathematical treatment [Baxter and Hardesty 1990].

Figure 61 Schematic illustration of chemical reaction on a tube in cross flow.

Both condensation and chemical reactions are strongly temperature dependent and give rise to spatial variation in ash deposit composition.

Experimental evidence of chemical reactions in deposits is presented in Figure 62, which is part of an analysis of chlorine-based corrosion. The top series of elemental maps are derived from a biomass (wheat straw) combustion test during which there was essentially no sulfur but significant alkali chloride present. The chlorides condensed primarily on the surface of the iron tube and initiated relatively rapid corrosion. When coal and biomass are combined, the sulfur

from the coal reacts with the alkali chloride on the tube surface to form an alkali sulfate (indicated here by the sulfur layer), which significantly slows the corrosion rate.

Figure 62 Illustration of the condensation of (potassium) chloride in the case of wheat straw combustion and the subsequent reaction of the chloride to form a sulfate when wheat straw and coal are cofired, leading to a significant decrease in corrosion rates.

Eddy Impaction $E(t, \tau)$

Eddy impaction is a process by which particles too small or light to inertially impact arrive at surfaces. They are deposited by the actions of turbulent eddies within or near the boundary layer rather than solely by their inertia as in inertial impaction. This process is less well understood than any of the previously discussed processes, and its description is tied to largely empirical coefficients. It influences only relatively small particles. One mathematical formulation that is fundamentally based is described above in connection with the effect of turbulence on inertial impaction rates. There are other largely empirical correlations. We have reviewed many correlations (all of which we are aware). Most formulations are empirical expressions based on conditions far removed from boilers (deposition on tube walls in isothermal flow) and most predict a greater deposition rate than the formulation indicated above. However, none of them predict a deposition rate that is significant compared to inertial impaction unless turbulence levels are assumed to be very high (10% of mean flow, for example). Generally, turbulence levels in boilers are less than 3% of the mean flow. However, fluid flow through tube bundles is

a complex and poorly understood phenomenon, and effective turbulence levels in such flows could be high.

Other Mechanisms

There are several other mechanisms of deposit growth other than those described above. Among these are electrostatic interactions, photophoresis, and Brownian motion. We have little evidence to suggest that these mechanisms contribute a significant amount of mass to the deposit and have chosen to ignore them in this formulation.

We have significant evidence that there is at least one mechanism that is important for submicron particles in addition to thermophoresis. Among the mechanisms discussed thus far, thermophoresis is the only one that is of importance for submicron particles. However, experimental verification of the rates of thermophoresis have not been satisfying when conducted under commercial conditions. As a deposit accumulates on a surface, the deposit surface temperature increases, which decreases the temperature gradient in the thermal boundary layer. Therefore, thermophoresis is expected to become less important as deposit thickness increases. Figure 63 illustrates how the thermophoretic driving force during one experiment decreased by a factor of about 5. All particles in this flow were submicron in size. However, the deposition rate on both the leading and trailing edges of the tube did not change, as indicated by the slope of the deposit thickness vs. time lines.

We have developed preliminary theories of this deposition mechanism that revolve around details of turbulent boundary layers. However, these theories have not yet been tested.

Figure 63 Illustration of the discrepancy between the thermophoretic driving force and the observed rate of deposition of submicron particles on a simulated heat transfer surface under commercial conditions.

Conclusions

This description of the model describes its current configuration. The predictions of the code are documented in a number of journal and conference proceedings articles [Abbott, Douglas et al. 1993; Baxter and DeSollar 1993]. The above discussion indicates that the model has a large number of areas that can be improved to increase its accuracy. However, the basic framework is sound and we do not anticipate that it will change for some time.

8. Particles and Clouds

Estimating particle concentrations as a function of particle size is fundamental to predictions of ash deposition. Each mechanism scales linearly with particle concentration at a given size. Therefore, estimation of particle concentrations represents a first-order term in predicting deposition rates. However, particle concentration fields are not easily computed. The particle models presented up to this point represent Lagrangian particle models, that is, they predict particle behavior as a function of starting conditions and starting time. Residence time is the dependent variable (together with starting time in non-steady flows). By contrast, the deposition models presume Eulerian particle information. That is, they require as parameters the concentration (and other properties) of particles as a function of space, not as a function of residence time. This section of the report describes a method of predicting particle properties and dispersion rates from Lagrangian models and translating the predictions to an Eulerian reference frame.

The fluid mechanics of most processes that entrain particles, droplets, or slurries as a dispersed phase in a gas stream are turbulent. Examples include spray drying, pneumatic transport of particles, heterogeneous chemical reaction/catalysis systems, and a large variety of internal and external combustion systems. The interactions of the condensed phases with the turbulent fluid mechanics in such systems are difficult to characterize. Characterization of the gas phase turbulence in itself is difficult, even in the absence of condensed phases. But the complications in describing the dispersion and reaction of the condensed phases in turbulent environments do not stem entirely or even primarily from the uncertainties in the description of the turbulence. Theoretical descriptions of the turbulent dispersion of particles and droplets are not well established, even when the characteristics of the gas-phase turbulence are known.

The focus of this section is the description of the transport of particles in turbulent gas flows. Throughout the discussion, the properties of the gas phase turbulence will be assumed known by assumption, experimental measurement, or from a model. Accurate measurements and models of turbulence properties in complex, developing flows are not generally available and the inaccuracies of available data and models will affect the results of turbulent transport modeling. However, the intent of this paper is to separate the gas phase turbulence modeling problem from particle transport in turbulent flows and explore a method of describing the latter if the former is well characterized.

Several reviews of turbulent particle dispersion document the progress in this area of research to date. Reviews of mixing and transport in turbulent environments and various aspects of the turbulent dispersion problem are available [Snyder and Lumley 1971; Goldschmidt, Householder et al. 1972; Lilly 1973; Hinze 1975; Chigier 1976; Crowe 1982; Faeth 1983; Shuen, Chen et al. 1983; Kuo 1986]. In terms of an analytical and comprehensive description of turbulent dispersion, Shuen and coworkers [Shuen, Chen et al. 1983] have shown modifications of the stochastic separated flow model (SSF) [Gosman and Ioannides 1981] that yield reasonably good predictions in a variety of flows and may represent the most rigorous technique currently available. The SSF model is based on a Monte-Carlo simulation of the particle flow field.

Several thousand trajectories are typically used to compute the overall particle or droplet behavior. The success of this approach is also dependent on a somewhat arbitrary choice of methods of evaluating its parameters. This and the host of other models suggested in the literature also depend on an accurate description of gas-phase turbulence.

The following discussion presents a description of turbulent particle dispersion that differs from currently employed models. This description is derived from theories of stochastic processes such as Brownian motion and classical turbulent dispersion models with established historical development [Taylor 1921; Taylor 1932; Taylor 1935; Taylor 1938; Batchelor 1949; Batchelor 1957; Csanady 1973]. The characteristics of the gas-phase turbulence are assumed to be known, either from experiment or from an appropriate model. Current gas turbulence models and experiments sometimes fall short of producing reliable estimates of turbulence properties in complex flows. The Stochastic Transport of Particles (STP) model uses classical properties of turbulence directly in its formulation and is independent of any particular turbulence model. The STP model will benefit from future improvements, and be limited by current inaccuracies, in the parameters used to characterize the properties of the flow.

This following discussion conceptually introduces the STP model, summarizes the mathematical equations on which it is based, compares its predictions with theory and data, and discusses implications of the results for particle dispersion generally.

Conceptual Illustration of the STP Model

The approach to describing turbulent particle dispersion in the STP model is to predict the statistics for the location of a cloud of identical particles released from a single point into a steady but inhomogeneous flow. Conceptually, the position of an individual particles is monitored as a function of residence time. Many such particles are released in sequence, generating a large number of particle position histories (trajectories). The statistics of these individual trials define a probability density function (pdf) for particles position that changes with residence time. This pdf is described in terms of time-dependent statistical parameters, such as the average particle position, the average standard deviation in particle position, correlation coefficients, and similar statistics.

Figure 64 presents an illustration of such a pdf early in residence time in an arbitrary two-dimensional flow field. The average particle position is near the origin, with a relatively small amount of dispersion about this mean. This represents the pdf shortly after the particles have been injected from a point source near the origin. Figure 65 illustrates the same particles later in residence time. The maximum value of the pdf is lower (note scale change on probability density axis) and the amount of dispersion is greater. The mean position is located at the (x,y) point of about (4.5,2). Figure 66 illustrates the pdf shortly before the mean leaves the flow field. Probability contour lines are superimposed on the bottom of this figure as a series of ovals. In this case, the extent of particle dispersion reaches completely across the flow domain in the y direction and well past the end of the flow domain in the x direction.

Figure 64 Illustration of the development of a Lagrangian pdf for particle position in an arbitrary coordinate system. At short residence times the mean particle location is near the point of injection (the origin in this case) as represented by the peak in the particle position pdf. The pdf is confined to a relatively small region of the flow domain. Flow is directed primarily in the + x direction. Compare with Figure 65 and Figure 66.

Figure 65 Illustration of the development of a Lagrangian pdf in an arbitrary coordinate system. At intermediate residence times the mean particle location is in a central region in the flow domain and the particle position pdf has nonzero values in a significant region of the flow domain. Compare with Figure 64 and Figure 66.

Figure 66 Illustration of the development of a Lagrangian pdf in an arbitrary coordinate system. At long residence times the mean particle location approaches the exit of the flow domain (flow is directed primarily in the + x direction) and the particle position pdf has nonzero values over most of the flow domain. Compare with Figure 64 and Figure 65.

A summary of the changing pdf is presented in schematic form in Figure 67. Here, each circle represents a contour line of the pdf at a different residence time. As is illustrated, the pdf gets continuously larger. The location of a typical Eulerian computational cell is also indicated in the figure. Several of the circles overlap the particular cell. This implies that particles of several different residence contribute to the overall particle contribution of the cell. The STP model tracks the time development of the pdf and the contributions to mass, momentum, and energy that the particles make within each computational cell.

In this paper, the basis for the time development of parameters describing the pdf is summarized. The implementation of the equations in a computational fluid dynamics model is completed [Baxter 1989], but not discussed here. The discussion here focuses on development of the model, illustration of important model predictions by comparison with other models and data, and discussion of implications of the results for modeling of turbulent particle dispersion generally.

Theoretical Discussion

The details of the stochastic model of turbulent particle dispersion, the STP model, are discussed in detail elsewhere [Baxter 1989]. The model is presented in summary form below in a form appropriate for a large number of experimental and theoretical conditions. The assumptions

Figure 67 A Lagrangian view of dispersion in a one dimensional flow. Each circle is a measure of the spatial extent of a pdf for particle position at successive times during the flow. The position of a typical Eulerian computational cell is also illustrated. Particles of many different residence times contribute to the overall population of particles in the cell.

required to derive these equations include (1) that the instantaneous particle and gas velocities are related through a linear differential equation (e.g., by Stokes' law), (2) that the correlation between particle number density and gas-phase velocity fluctuations is known, (3) that the mean and fluctuating components of the gas velocities are known everywhere in the flow field, and (4) that the turbulent properties change in the flow field at a rate comparable to or less than the relaxation time of the particles. One of the driving forces for this work is the description of the particle phase in relatively comprehensive pulverized coal combustion models. Assumptions 1 and 4 are well justified under these conditions (small particles with modest density dispersed in modestly turbulent, essentially steady-state gas flows). The supposition in developing the STP model is that the gas phase can be described either by experiment or, more commonly, by a computational fluid dynamics model that is to be coupled with the STP model. Assumption number 3, the coupling between particle concentrations and gas-phase velocity fluctuations, addresses a level of detail rarely available from either experiment or modeling. The assumption commonly used in applications of the STP model is that there is no correlation between the two. This is an oversimplification, particularly in the early stages of particle dispersion, for many conditions. However, there appear to be no reasonable alternatives in most applications of the model. Relaxation of all of these assumptions can be done within the framework of the STP model without great difficulty if sufficient detail is known about the gas-phase behavior, as is discussed elsewhere [Baxter 1989]. The discussion here focuses on application of the model within the limitations of commonly used descriptions and measurements of gas-phase turbulence, i.e., turbulence models or data that detail mean gas-phase velocities and the rms values of their fluctuations as a function of position and time.

General Equations for the STP Model

The STP model describes particle dispersion as a stochastic process, and its equations describe statistical properties of the dispersion process. In particular, the equations describe the mean and covariance matrix for particle position as a function of particle residence time, designated t_2 . The time of release of particles is given as t_1 . Transient processes and individual particle motion are functions of both t_1 and t_2 . For steady (statistically stationary) flows, the mean and covariance matrix for particle position are dependent on particle residence time but not on the time at which particles are released. The equation for mean particle position is

$$\langle x_i(t_1, t_2) \rangle \equiv \int_0^{t_2} \langle u_i(t_1, t_2) \rangle dt + \langle x_i(t_1, t_2 = 0) \rangle \quad (77)$$

where x and v represent position and velocity, respectively, and angle brackets represent ensemble average values. Traditional indicial notation is used to represent the particle position vector, with subscripts i and j representing coordinate directions here and elsewhere. In Eq. (77), x_i represents the position vector of an individual particle and is a function of both t_1 and t_2 . The ensemble average of x_i is an average with respect to time of release (t_1) and depends only on residence time (t_2).

The particles whose positions are represented by x_i in Eq. (77) can be either fluid particles or macroscopic particles. Macroscopic particle properties are represented hereafter by a subscript p , which is separated from the indicial subscripts i and j by a semicolon. The equation of motion for macroscopic particles is given by

$$\frac{du_{i;p}}{dt_2} \equiv \beta(t_2)(u_{i;g}(t_1, t_2) - u_{i;p}(t_1, t_2)) + A_i(t_1, t_2) + g_i \quad (78)$$

where β represents the exchange coefficient, A represents random forces normalized by particle mass such as molecular collisions (which give rise to Brownian motion), g represents the acceleration of gravity (or any other body forces normalized by mass), and the other terms have been previously defined. In many practical cases, the exchange coefficient is independent of particle and gas velocity. For example, for particles that obey Stokes' law the exchange coefficient is given by $3\pi d_p \mu_g / m_p$. The residence-time dependence of the exchange coefficient accounts for the changes in particle mass and diameter and gas viscosity (temperature and composition) for reacting particles in a reacting flow. Release-time dependence of the exchange coefficient is ignored in Eq. (78); identical particles are assumed to be released into a fluctuating velocity field, but changes in the velocity field are assumed to have no impact on the exchange coefficient.

Equation (78) contains few assumptions for non-reacting particles in isothermal flows. Additional terms can be added to Eq. (78) to describe virtual mass, thrust, Magnus, Bassett, and Saffman forces, buoyancy, etc. [Crowe 1979; Kuo 1986]. The combined contributions of these terms is small (typically less than 1 %) in most practical applications [Baxter 1989], so they are neglected

in the remaining discussion here. In applications where they are significant, they could be included without change in the general approach to the problem.

The ensemble average of Eq. (78) provides a basis for calculating the mean particle position. Particle clouds with exchange coefficients that are uncorrelated with initial time, particle velocity, and gas velocity exhibit mean positions given by

$$\frac{d\langle u_{i,p}(t_1, t_2) \rangle}{dt_2} \equiv \beta(t_2) \left(\langle u_{i,g}(t_1, t_2) \rangle - \langle u_{i,p}(t_1, t_2) \rangle \right) + \langle A_i(t_1, t_2) \rangle + g_i \quad (79)$$

This equation is valid only when fluctuations in are uncorrelated with those in either the gas or the particle velocity. This includes all particles in the Stokes' regime and many particles outside of it. In cases where this simplification can not be made, the averaging must be done over the entire first term on the right side rather than over the two velocity components separately. Residence-time variations in the exchange coefficient are assumed to be independent of release-time variations in gas properties in Eq. (79) from this point on. The ensemble average of the gas velocity can be calculated from its expected value, given by

$$\langle u_{i,g}(t_1, t_2) \rangle = \frac{\iiint_{x_i \pm \infty} \langle u_{i,g}(x_i, t_1, t_2) \rangle \langle n(x_i, t_1, t_2) \rangle dx_i}{n_T} \quad (80)$$

where n represents particle number density. This is not the same as the average gas velocity at the mean particle position, although the latter can be shown to be a leading term in the calculation. That is,

$$\langle u_{i,g}(t_1, t_2) \rangle \neq u_{i,g}(\langle x_i \rangle, t_1, t_2) \quad (81)$$

Ensemble average values for the components of the random force can be similarly computed. The difference between these means and the instantaneous values of the corresponding variables is designated by a prime and represents a perturbation from the mean. For a generic vector v ,

$$v_i(t_1, t_2) = \langle v_i(t_1, t_2) \rangle + v'_i(t_1, t_2) \quad (82)$$

This decomposition of the variables differs in concept and magnitude from the Reynolds and Favre averages of Eulerian properties discussed in most turbulence literature. Equation (82) includes an ensemble average, or expected value, of a Lagrangian variable for a cloud of particles. This ensemble average is computed by conducting an experiment with many different release times and averaging the results as a function of residence time. Such an average is mathematically identical to the expected value, which is computed by integration over a pdf, as indicated in Eq. (81). The ensemble average is independent of release time if the Eulerian flow variables are stationary (flow is at steady state). The Reynolds- and Favre-averaged quantities in most turbulence literature relate to point measurements. These averages result from time

averaging the variable (Reynolds average) or the product of the variable and the density (Favre average) at one point in space.

The solution to Eq. (79) yields the mean velocity of the particle cloud, the integral of which defines the mean position. The covariance matrix defines the rate of cloud expansion. The time rate of change of the particle velocity covariance tensor is computed by ensemble averaging the product of the position perturbations. The result yields

$$\frac{d\langle X'_{i,p}(t_1, t_2) X'_{j,p}(t_1, t_2) \rangle}{dt_2} = \int_0^{t_2} \left\{ \langle u'_{i,p}(t_1, \tau) u'_{j,p}(t_1, t_2) \rangle + \langle u'_{j,p}(t_1, \tau) u'_{i,p}(t_1, t_2) \rangle \right\} d\tau + \langle X'_{i,p}(t_1, t_2 = 0) u'_{j,p}(t_1, t_2) \rangle + \langle X'_{j,p}(t_1, t_2 = 0) u'_{i,p}(t_1, t_2) \rangle \quad (83)$$

Particles released from a point source have variations in the position of particle release, $X'_{i,p}(t_1, t_2 = 0)$, of zero. Under these common conditions, the last two terms in Eq. (83) equate to zero.

Normalization of the velocity correlations in Eq. (83) by $\langle u'^2_{i,p}(t_1, t_2) \rangle^{1/2} \langle u'^2_{j,p}(t_1, t_2) \rangle^{1/2}$ and defining a normalized Lagrangian correlation tensor as

$$R^L_{ij,p}(\tau, t_2) \equiv \frac{\langle u'_{i,p}(t_1, \tau) u'_{j,p}(t_1, t_2) \rangle}{\langle u'^2_{i,p}(t_1, t_2) \rangle^{1/2} \langle u'^2_{j,p}(t_1, t_2) \rangle^{1/2}} \quad (84)$$

(where no summation is intended with respect to subscripts) yields

$$\frac{d\langle X'_{i,p}(t_1, t_2) X'_{j,p}(t_1, t_2) \rangle}{dt_2} = \langle X'_{i,p}(t_1, t_2 = 0) u'_{j,p}(t_1, t_2) \rangle + \langle X'_{j,p}(t_1, t_2 = 0) u'_{i,p}(t_1, t_2) \rangle + \int_0^{t_2} \left\{ \langle u'^2_{i,p}(t_1, t_2) \rangle^{1/2} \langle u'^2_{j,p}(t_1, t_2) \rangle^{1/2} (R^L_{ij,p}(\tau', t_2) + R^L_{ji,p}(\tau', t_2)) \right\} d\tau' \quad (85)$$

Equations (85) and (83) are sufficient expressions for the time dependence of the variance in particle position. Neither equation is very useful, however, since the joint velocity correlations are not clearly related to gas properties or known particle properties.

A useful relationship between the correlations in Eqs. (85) and (83) and known properties can be developed. Subtracting Eq. (79) from Eq. (78) yields an expression for the residence-time variation in the perturbation velocity as a function of particle and gas properties.

$$\frac{d u'_{i,p}(t_1, t_2)}{dt_2} = \beta(t_2) (u'_{i,g}(t_1, t_2) - u'_{i,p}(t_1, t_2)) + A'_i(t_1, t_2) \quad (86)$$

The general solution to this equation can be written as

$$u'_{i,p}(t, \tau) = \exp \left[\int_0^\tau \beta(t') dt' \right] \left\{ u'_{i,p}(t, 0) + \int_0^\tau \beta(t') u'_{i,g}(t, t') + A'_i(t, t') \exp \left[\int_0^{t'} \beta(t'') dt'' \right] dt' \right\} \quad (87)$$

where $u'_{i,p}(t, 0)$ represents the initial particle velocity perturbation and $\tau = t_2 - t_0$. Variables of integration are indicated by either single or double primes in Eq. (87). The ensemble average of the product of Eq. (87) and $u'_{j,p}(t_1, t_2) / \langle u'^2_{i,p}(t_1, t_2) \rangle^{1/2} \langle u'^2_{j,p}(t_1, t_2) \rangle^{1/2}$ yields

$$R^L_{ij,p}(\tau, t_2) \equiv \frac{\langle u'_{i,p}(t_1, \tau) u'_{j,p}(t_1, t_2) \rangle}{\langle u'^2_{i,p}(t_1, t_2) \rangle^{1/2} \langle u'^2_{j,p}(t_1, t_2) \rangle^{1/2}} = \exp \left[\int_0^\tau \beta(t') dt' \right] \left\{ \frac{\langle u'_{i,p}(t_1, 0) u'_{j,p}(t_1, t_2) \rangle}{\langle u'^2_{i,p}(t_1, t_2) \rangle^{1/2} \langle u'^2_{j,p}(t_1, t_2) \rangle^{1/2}} + \int_0^\tau \frac{\beta(t') \langle u'_{i,g}(t_1, t') u'_{j,p}(t_1, t_2) \rangle}{\langle u'^2_{i,p}(t_1, t_2) \rangle^{1/2} \langle u'^2_{j,p}(t_1, t_2) \rangle^{1/2}} + \frac{\langle A'_i(t_1, t') u'_{j,p}(t_1, t_2) \rangle}{\langle u'^2_{i,p}(t_1, t_2) \rangle^{1/2} \langle u'^2_{j,p}(t_1, t_2) \rangle^{1/2}} \exp \left[\int_0^{t'} \beta(t'') dt'' \right] dt' \right\} \quad (88)$$

This defines the normalized Lagrangian particle correlation function. Some limiting forms of the equation will be considered, concluding with one that is applicable to the type of information available from common, two-equation turbulence models.

Markovian Approximation

The Lagrangian velocities are stationary with respect to residence time if the flow field is homogeneous and the particles are injected at their equilibrium velocities. One property of stationary variables is that their correlations, such as R^L , are even functions of the difference in time, τ , and independent of (residence) time itself [Papoulis 1984; Gardiner 1985]. A residence time of zero is a particularly convenient choice for evaluating t_2 . The rms perturbations are also independent of residence time in a homogeneous turbulence field. If the magnitudes of the correlations of particle with gas velocity and with random perturbations decay instantly, a classical Markovian system [Ethier and Kurtz 1986] obtains in which

$$R^L_{ij,p}(\tau) \equiv \frac{\langle u'_{i,p}(\tau) u'_{j,p}(0) \rangle}{\langle u'^2_{i,p} \rangle^{1/2} \langle u'^2_{j,p} \rangle^{1/2}} = \exp \left[\int_0^\tau \beta(t') dt' \right] \frac{\langle u'_{i,p}(0) u'_{j,p}(0) \rangle}{\langle u'^2_{i,p} \rangle^{1/2} \langle u'^2_{j,p} \rangle^{1/2}} \quad (89)$$

where τ is used to represent residence time difference. For the principal diagonal of this tensor ($i = j$) the second factor on the right becomes unity and Eq. (89) defines the autocorrelation function, which is seen to be an exponential decay. This classical result relates to early progress in describing Brownian motion (effect of A is ignored).

Fluid Particle (Gas) Dispersion

If the particles are assumed to be fluid particles ($\beta \rightarrow \infty$) dispersing in a homogenous flow field,

$$R_{ij,p}^L(\tau) \equiv \frac{\langle u'_{i,g}(t_1, \tau) u'_{j,g}(t_1, 0) \rangle}{\langle u'^2_{i,g} \rangle^{1/2} \langle u'^2_{j,g} \rangle^{1/2}} = R_{ij,g}^L(\tau) \quad (90)$$

In nonstructured turbulence, the autocorrelation function for the gas can also often be approximated by an exponential decay. These results relate to turbulent dispersion work initiated by Taylor and carried on by others [Taylor 1921; Taylor 1932; Taylor 1935; Taylor 1938; Batchelor 1949; Batchelor 1957].

Parameter Definition for two-equation turbulence models

Two-equation descriptions of turbulence such as the k - ϵ model predict a turbulent kinetic energy and a decay rate. If the particles are entrained in a gas with velocity fluctuations of frequency s and exponentially changing magnitude with time constant $1/r$, then the following relationship exists between the magnitude of the rms velocity fluctuations of the gas and particles under fairly general assumptions [Baxter 1989]

$$\frac{\langle u'^2_{i,p}(t_1, t_2) \rangle \sigma^2_{i,u_p}}{\langle u'^2_{i,g}(t_1, t_2) \rangle \sigma^2_{i,u_{gp}}} = \frac{\beta^2}{(\beta + r)^2 + s^2} \quad (91)$$

This result assumes that the decay rate, r , is slow enough that the particles experience several fluctuations before the turbulence becomes zero. The rate of change of turbulent intensity, r , is negative if the turbulence is decaying. The predictions of Eq. (91) in the limits of small and large particles and in the limits of homogeneous and inhomogeneous turbulence are as follows: (1) large particles ($\beta \ll s$) in nearly homogeneous flows ($\beta \ll |r|$) are not significantly impacted by gas phase fluctuations; (2) small particles ($\beta \gg s$) in nearly homogeneous flows ($\beta \ll |r|$) are dominated by gas phase fluctuations; (3) all particles in decaying turbulent flow fields ($r < 0$) have the potential of exhibiting gas-phase induced velocity fluctuations greater than those of the gas in the local region.

If the residence time dependence of the gas-phase correlations scales with turbulent intensity and the effects of random forces are ignored, the correlation function can be simplified for use in typical turbulence models. The influence of the molecular bombardment on the particles is small compared with that of the gas fluctuations and is ignored. These assumptions allow an approximate form of the correlation function to be written as

$$\frac{d\langle x'_{i,p}(t_1, t_2) \rangle}{dt_2} = \int_0^{t_2} \left\{ 2\langle u'_{i,g}(t_1, t) \rangle \frac{\frac{\beta^2}{(\beta + r)^2 + s^2} + \int_0^t \beta R_{i,g}^L(t') \exp\left[-\int_0^{t'} \beta(t'') dt''\right] dt'}{\exp\left[-\int_0^t \beta(t'') dt''\right]} \right\} dt \quad (92)$$

where all particles are assumed to be injected in the flow from a point source at $x = 0$ and at residence time zero. No summation of indices is implied. The off-axis components of the covariance tensor are ignored if no information on correlations between different velocity components is available, as is usually the case for simple turbulence models.

The gas correlation function is also typically not available. In such cases, a Markovian approximation is made for the gas as follows

$$R_{i,g}^L(t) \equiv \exp\left[-\int_0^t \tau_g(t') dt'\right] \quad (93)$$

where

$$\tau_g = \frac{C_\mu^{3/4} k^{3/2}}{\varepsilon \left(\frac{2k}{3}\right)^{1/2}} \quad (94)$$

The mean and variances of the pdf are now fully specified, and the information available from the gas-phase turbulence model is exhausted. Given more information, the off-axis components of the covariance matrix and possibly higher-order moments of the mean could be specified. However, there are theoretical reasons to believe that the pdf eventually becomes a multivariate normal distribution, in which case the mean and covariance matrix are all that is required to fully specify it. The information at hand should be a reasonable approximation to the actual rate of dispersion.

The description of particle dispersion presented above differs from classical analyses that invoke diffusion coefficients. Such diffusion coefficients, and the associated concentration gradients, are not used in this model. Since the complete solution to the dispersion problem is available, the diffusion coefficient could be calculated from the results of this model. Such a calculation results in

$$D_{i,p}^*(t_2) = \frac{1}{2} \int_0^{t_2} \left\{ \langle u'^2_{i,p}(t_1, t_2) \rangle^{\frac{1}{2}} \langle u'^2_{i,p}(t_1, t_2) \rangle^{\frac{1}{2}} R_{i,p}^L(t, t_2) + \langle u'^2_{i,p}(t_1, t_2) \rangle^{\frac{1}{2}} \langle u'^2_{i,p}(t_1, t_2) \rangle^{\frac{1}{2}} R_{i,p}^L(t, t_2) \right\} dt \quad (95)$$

This diffusion coefficient is the proportionality constant between the negative of the local particle concentration gradient and the local particle mass flux. However, it has several properties that are not normally associated with diffusion coefficients. For example, it has a clear time dependence in all cases where particles are injected from a point source. It is also potentially negative valued (see Figure 71). Finally, it can not be calculated from local conditions in the flow alone. The asterisk is used to distinguish this coefficient from the more classical concept. The reasons for these differences are discussed later.

Comparison of Results with Analytical and Experimental Data

The STP model has been compared with analytical and experimental data. In all cases, the environment in which the particles are dispersing is either well characterized or, in the case of the analytical results, precisely defined. This has the advantage of ensuring that the comparisons reflect dispersion calculations rather than ability to model or measure turbulent environments. It has the disadvantage of being limited to very simple flow configurations. The purpose in performing the comparisons is to develop insight into the dispersion process generally.

The solution to the diffusion equation is well established under the conditions of a point source with a constant velocity in one direction and a constant (and known) diffusion coefficient. This solution has been used by others to evaluate particle dispersion models. Results from two such models (SSF 1 and SSF 2) are shown in Figure 68 together with the analytical results (shown as points) and the prediction of the STP model (indicated by the authors' names) [Gosman and Ioannides 1981; Shuen, Chen et al. 1983].

Figure 68 Comparison among several particle dispersion models and an analytical solution.

Specification of the distance and time between random velocity perturbations is the principal difference between the two SSF models. The two stochastic separated flow (SSF) models indicated are similar in some respects to the STP model except that the statistical averaging is done by launching particles into the flow stream and integrating their trajectories in a Monte Carlo fashion. Results from many trajectories are averaged. By comparison, the STP model averages the equations to produce a statistical description of the cloud of particles. The advantage to the SSF approach is that nonlinearities in the equations can be dealt with more accurately than in the STP model. The advantages to the STP approach are computational efficiency and formalized relationships between gas and particle turbulence properties. The principal weakness of both models is a lack of detailed gas turbulence data (Lagrangian velocity covariance tensors, for example).

In this idealized case, where diffusion coefficients are constant and known, the STP model predicts the analytical result. The value of the integrand in Eq. (95) eventually becomes zero, and integral is a constant. This constant is the diffusion coefficient. If the integrand is adjusted such that it rapidly decreases to zero and its integral has the proper magnitude, the STP model produces the same result as the analytical solution. The result is obtained in a single simulation of a particle cloud. Monte Carlo techniques, by their very nature, require several thousand trajectory calculations to produce a well-behaved solution. A cloud simulation requires about three times as much computational effort as a single Monte Carlo trajectory calculation.

The value of the mean particle position is easily computed in a homogeneous, uniform flow. To a large extent, turbulent particle dispersion is predicted by time development of the covariance matrix. A second set of data that characterize this time development are derived from dispersion of liquid in liquid (no slip velocity) [Kalinske and Pien 1944]. These data are illustrated in Figure 69. The data represent the cross-stream variance in particle position as a function of normalized time for a large number of different flow conditions. The normalization constant is the integral time scale, which is the area under the R_{ij} curve between the point of release and the time the curve becomes identically zero.

Assuming a Markovian autocorrelation function parameterized by this (measured) time constant and homogeneous flow leads to an analytical solution to the time development of the variance. This function is given by

$$x_{ij}'^2 = 2v_{ij}'^2 \left\{ \frac{t_2}{\tau} - \frac{1}{\tau^2} [1 - \exp(-\tau t_2)] \right\} \quad (96)$$

where τ represents the integral time scale. This function is illustrated, together with the data in Figure 69. Both data and function were normalized by the rms velocity fluctuations and measured integral scales were used to normalize the data.

Figure 69 Comparison of fluid particle dispersion exhibiting Markovian-type dispersion. The diffusion coefficient is proportional to the slope of the data and clearly time dependent.

A close examination of Eq. (95) indicates that the diffusion coefficient is proportional to the derivative of the variance, or more properly, the tensor components are proportional to the derivative of the covariance tensor. The data in Figure 70 show that this diffusion coefficient is clearly time dependent up to a normalized time of about 2.5, even though the flow is essentially homogeneous. A turbulence model that bases its calculations on the values of local variables alone could not capture this effect. The agreement between the data and the STP model results from (1) modeling the process in a physically meaningful way, and (2) having access to accurate turbulence properties.

The time dependence of the dispersion process and diffusion coefficient are closely related to the time dependence of R_{ij} . In the absence of better information, the STP model uses the Markovian approximation for R_{ij} . Classical data under well-characterized conditions are available to evaluate the adequacy of this assumption. Figure 70 illustrates the measured values of autocorrelations for particles with a range of relaxation times (1.7 to 49 msec) dispersing in a well-characterized field of grid turbulence [Snyder and Lumley 1971]. The data are all normalized with the respective measured integral scales of the particles. Also indicated in the figure is the Markovian autocorrelation function. There are minor differences between the Markovian autocorrelation function and the data. In particular, the data indicate a slightly negative value between the normalized times of 4 and 6. The Markovian exponential decay is nonnegative and monotonically decreasing. Aside from these minor differences, the agreement is good.

Figure 70 Comparison of particle autocorrelation functions, normalized by measured integral scales, and the Markovian autocorrelation. The diffusion coefficient is residence time dependent until the autocorrelation function becomes identically zero.

Implications for Particle Dispersion Generally

Most flow environments of practical concern contain shear layers, recirculation zones, and other features that make the dispersion problem much more complicated than in those discussed in the previous section. If the details of the gas turbulence field are known, the STP model offers a reasonably rigorous approach to predicting the particle dispersion. In most cases, the gas flow is not well characterized. However, the results from the comparisons with the simple flows previously discussed allow some comment to be made on the general nature of particle dispersion in the great majority of practical flows.

Classical Fickian diffusion asserts that a diffusion flux is proportional to a concentration gradient and a diffusion coefficient, the latter being independent of residence time in a steady flow. The data and theory previously presented indicate that turbulent particle dispersion cannot be described by such an approach until the correlation tensor decays to a steady value of zero. The integral time scale is an indication of the time required before a group of initially concentrated particles is no longer influenced by their initial conditions and the correlation tensor decays to zero. In most combustion flows, this integral time scale is on the order of one second. This is long compared to other time scales of interest in such flows. Therefore, most of the relevant dispersion occurs before the diffusion coefficient becomes independent of time.

There are several indications of more complex dispersion. One of the most vivid is counter-gradient diffusion. The physical origins of counter-gradient diffusion are difficult to appreciate when viewed from a reference frame of Fickian diffusion. If viewed from the statistics of

turbulent fluctuations, Eq. (88) shows how negative gas-phase velocity correlations can cause the particle correlation function to become negative. If the magnitude and length of the negative correlation is sufficient to cause the integral in Eq. (95) to become negative, counter-gradient + diffusion results. An illustration of such behavior is included as Figure 71.

Figure 71 Illustration of the behavior of a diffusion coefficient based on a Markovian process and the diffusion coefficient from more complicated flows, in this case exhibiting counter-gradient diffusion.

The residence-time dependence of the correlation function complicates the description of particle dispersion from an Eulerian reference frame. Figure 72 illustrates an example where particles are injected at two points separated in time by less than the integral scale of the turbulence. Under such conditions, identical particles at identical locations in identical environments will exhibit different diffusion coefficients because of this residence-time dependence. Therefore, particle dispersion under such conditions cannot be described as a function of local properties only.

Figure 72 Illustration of the significance of a time dependent diffusion coefficient in making Eulerian calculations of particle dispersion. Identical particles in identical environments exhibit different diffusion coefficients at the same location because of the residence-time dependence of the correlation functions.

Conclusions Regarding Particle Concentration Profiles

An approach to describing particle transport in turbulent flows has been demonstrated based on an extension of stochastic process modeling and turbulence theory. The model requires no adjustable parameters beyond specification of the turbulent flowfield itself and is independent of any particular turbulence model. Approximations for the parameters required in the model are presented in terms of parameters from the $k-\epsilon$ gas-phase turbulence model and particle properties. This stochastic transport of particles (STP) model does not depend on specification of diffusion coefficients or concentration gradients. Indeed, the model indicates that diffusion coefficients in turbulent flows typically are time dependent for times long relative to many important process time constants. A variety of flows exhibit this time dependence. For simple, unstructured flows, a Markovian approximation is shown to represent the correlation function adequately. For more complex flows, the STP model can take advantage of more detailed gas-phase turbulence parameters and predict, for example, counter-gradient diffusion. Implications of the results for turbulent dispersion generally are also discussed.

9. Deposit Properties and Property Algorithm Development

This section summarizes deposit properties and the algorithms used to describe these. The properties of primary interest are emissivity, absorptivity, reflectance, thermal conductivity, viscosity, and strength. Deposit thermal conductivity is discussed in detail in the appendix and is only briefly discussed here. Radiative properties (emissivity, absorptivity, and reflectance) are discussed here in some detail, followed by a briefer discussion of the remaining properties. This section also includes a discussion on the impact of such properties on boiler operation.

Emissivity and Absorptivity of Deposits

This section of the discussion describes emission and reflection from a particulate layer assuming that the behavior of an individual particle in that layer is known. The scattering of a particle that has near neighbors differs from that of an isolated particle – sometimes by large amounts. An appreciation for the different behaviors can be quickly acquired by considering the large particle size limit of scattering efficiencies. It is well known that many particles scatter twice the amount of light as is incident on their geometric cross section as the particle size becomes large. At smaller sizes, the amount of scattering may either exceed a factor of two (sometimes by a large margin), or approach zero.

If particles in close proximity behaved similarly, they would, as a group, scatter twice the light as is incident on the layer. This violates conservation of energy principles. Clearly, the presence of other scatterers in the vicinity of a particle influences the particles' scattering behavior. The radiative transport equation is the point of departure for describing radiative transfer through arbitrary media:

$$\frac{\partial I(s, \Omega)}{\partial s} = -E(s, \Omega)I(s, \Omega) + \frac{1}{4\pi} \int_{4\pi} I(s, \Omega') G(s, \Omega, \Omega') d\Omega' + F(s, \Omega) \quad (97)$$

where I represents the radiance of a beam, s represents distance of path length, Ω represents direction, E represents the volume extinction coefficient, G represents the volume angular scattering coefficient, and F represents the volume emission coefficient.

This integrodifferential equation does not lend itself to solution by systematic means. The *ad hoc* solutions that do exist are not of particular practical relevance. The equation can be simplified somewhat for the case of horizontally stratified media, but it does not reduce to a form that has a known general analytical solution.

If we assume the particulate layer is semi-infinite and homogeneous, a solution to the radiative transport equation follows from an analysis of scattering in the media. Under these assumptions, it should make no difference to the emissivity or reflectivity if a thin layer of particles is added or removed from the surface of the layer. The solution to the equation is found by requiring that the expression for the reflectance and emission from the original layer be equal to that of the surface after the layer is removed. Figure 73 illustrates the situation for the case of the bi-directional reflectance. The five first-order changes in the reflectance associated with adding a thin layer of

Figure 73 Schematic illustration of the solution of the radiative transport equation.

particles to the surface are illustrated as: (a) reduction in intensity by extinction of the light as it passes through and returns through the layer; (b) scattering of the new layer toward the observer; (c) light scattered from the new layer being backscattered from underlying material; (d) light scattered from the lower medium illuminating the new layer and adding to the observed reflectance; and (e) light twice scattered between the new layer and the original layer illuminating the old layer. The sum of these five effects must be zero.

Within the constraints of isotropic, independent scatterers (the assumptions of this analysis), the radiative transport equation yields an exact solution given by

$$r(i, e, g) = \frac{w}{4\pi} \frac{\mu_o}{\mu_o + \mu} H(\mu_o) H(\mu) \quad (98)$$

where

$$H(x) = 1 + \frac{w}{2} x H(x) \int_0^1 \frac{H(x')}{x + x'} dx' \quad (99)$$

and i , e , and g represent the zenith angles of incidence, emergence (observation), and the phase angle, respectively, w represents the volume single-scattering albedo, and μ and μ_o represent the cosines of e and i , respectively.

The function H is obviously somewhat awkward to calculate, but it is analytical and there are several good approximations to it. The surface emissivity can be similarly derived or calculated by difference from the incident beam and the reflectivity. The problem of computing the reflectivity or emissivity has been reduced to calculation of the parameter w and geometrical quantities. Additional complications include the opposition effect, a surge in reflectivity as i and e approach one another, and inhomogeneous or nonspherical particles. The opposition effect can be treated analytically. Other effects can be approximated within reason. The details of these approaches are lengthy and are not presented here.

A computer algorithm for predicting the reflectivity and emissivity of particulate layers according to this theory was completed this quarter. This algorithm is sensitive to multiple scattering, porosity, composition, and particle size. We are currently seeking ways to validate it analytically and experimentally. An example prediction is indicated in Figure 74.

The predictions indicate the bi-directional reflectance as a function of angle of incidence of light on a surface composed of particles with two different optical constants characterized by the albedo factor. The square of the albedo factor is equal to one minus the volume single scattering albedo. High albedo factors represent absorbing particles whereas low albedo factors represent scattering particles.

The figure illustrates the primary sensitivity of reflectance is to the optical properties of the particles, with lesser sensitivities to the porosity of the layer or the size of the particles. There is far less sensitivity to size *per se* except as size impacts scattering properties. The peak in reflectance occurs near the angle of incidence (60°) and is called an opposition effect. This effect

is sensitive to porosity but less sensitive to size directly. Small particles often form particulate layers that are highly porous, yielding a functional dependence on size that is stronger than the mathematical dependence.

Figure 74 Illustration of the bi-directional reflectance as a function of angle of incident light for particles of significantly different scattering properties. The peak illustrated at about 1 radian is associated with an intense back scatter from granulated material known as the opposition effect.

Recent literature discussing deposit radiative properties indicates their dependence on chemical composition and structure [Goodwin 1986; Wall, Bhattacharya et al. 1994]. Most ash deposits show spectral variation in their emissivity as a function of wavelength. The spectral dependence is due in part to deposit composition and in part to deposit morphology. This variation gives rise to a temperature-dependent total or effective emissivity, as is illustrated for coal and char particles in our earlier work [Baxter, Fletcher et al. 1988] and for ash deposits in more recent work [Richards, Logan et al. 1992; Baxter 1993; Baxter, Richards et al. 1993; Richards, Slater et al. 1993; Wall, Bhattacharya et al. 1994]. The FTIR emission spectroscopy diagnostic developed at Sandia for measuring surface species composition is also suitable for measuring ash deposit spectral emissivity over the range from about 3 to 20 μm . The strong dependence of emissivity on deposit morphology indicates that the most meaningful measurements will be obtained from an *in situ* device. That is, preparation of deposits for post mortem analyses often alters their

structure. In addition, removing them from the combustion zone often alters the details of their chemistry and morphology.

Quantitative measurements of deposit emissivity are available in the literature. Deposit emissivity is shown to increase with increases in particle size in the deposit, up to at least 400 μm . Emissivity is also profoundly affected by the presence of atoms that form mixed silicates, sometimes referred to as coloring agents [Boow and Goard 1969]. More formal relationships between composition and emissivity have been investigated [Goodwin 1986], and experimental data illustrating the dependence of emissivity on structural properties [Markham, Best et al. 1992] have been reconciled with published theoretical treatments indicating similar trends [Bohren and Huffman 1983]. Systematic studies of specific constituents of ash deposits as a function of composition and temperature and of ash deposits directly have also been presented, although particle size and morphology effects are not typically addressed [Mitor and Konopel'Ko 1966; Mitor and Konopel'Ko 1970; Mitor and Konopel'Ko 1970; Street and Twamley 1971; Vassallo, Cole-Clarke et al. 1992; Vassallo and Finnie 1992]. Industrial experience with deposits has documented the effect of deposit emissivity on pollutant production, boiler derating, convection pass fouling, and other operational issues and indicates that deposit-emittance-based boiler diagnostics can be successful in anticipating the problems [Mulcahy, Boow et al. 1966; Mulcahy, Boow et al. 1966; Goetz, Nsakala et al. 1979; Carter and Koksall 1991; Carter, Koksall et al. 1992]. Deposit emissivity and absorptivity depend strongly on both morphology and composition. Morphological considerations include porosity, shape, and thickness. Porosity is the dominant morphological factor if it is defined broadly, i.e., to include particle size and pore size information. The effect of porosity can be large. For example, weakly absorbing materials develop high hemispherical reflectivities when ground to a fine particle size and spread over a surface. Analytical approaches for describing such phenomena are available in the literature at several levels of approximation [Bohren and Huffman 1983; Goodwin 1986; Wall, Bhattacharya et al. 1994].

Thermal Conductivity of Deposits

Thermal conductivity of ash deposits represents the second major variable controlling heat transfer rates in boilers. This topic is discussed in detail in the Appendix, together with measurements from the MFC and a complete theoretical development. The potentially complex chemical species formed in ash deposits do not all have conductivities with well-known dependencies on temperature. However, the greatest source of uncertainty in predicting thermal conductivities is associated with the deposit microstructure and porosity. Heat transfer through porous media can more than an order of magnitude less efficient through many boiler deposits than it would be through non-porous samples of the same composition.

Thermal conductivity has been observed to increase with increasing particle size and, in the case of fine, non-sintered dusts, to approach the value of air [Boow and Goard 1969]. Detailed investigations of heat transfer through porous media have been completed at Sandia, together with development of experimental techniques for measuring thermal conductivity in situ in the MFC. Additionally, theoretical analyses of deposit microstructure [Tassopoulos, O'Brien et al. 1989; Tassopoulos and Rosner 1992; Tassopoulos and Rosner 1992; Tassopoulos and Rosner 1992; Tassopoulos and Rosner 1992] and its effect on transport properties have been completed.

Experimental data describing thermal conductivity dependencies on both morphology and composition are also available from practical systems [Mulcahy, Boow et al. 1966; Mulcahy, Boow et al. 1966; Anderson, Viskanta et al. 1987]. Fundamental approaches to describing the thermal conductivity based on detailed knowledge of ash deposit structure are available [Jagota, Dawson et al. 1988; Jagota and Hui 1990; Tassopoulos and Rosner 1992; Tassopoulos and Rosner 1992]. The appendix records our contribution to this field in some detail, a few highlight so which are indicated here.

Deposit Strength, Tenacity, and Resistance to Thermal Shock

Ash deposition on heat transfer surfaces is inevitable in essentially all coal combustors. Successful management of these deposits in dry-walled units by soot blowers, wall blowers, or water lances is critically dependent on the deposit strength, tenacity, and thermal shock resistance. Definitions for these terms as used in this document are quite precise. As described earlier, strength relates to the bulk deposit and represents its ability to resist stress without plastic or catastrophic deformation. Tenacity is a similar property, but relates to the interface between the deposit and a surface. Thermal shock resistance is a combination of a thermal expansion coefficient, which indicates the magnitude of a stress generated in a deposit as a consequence of a temperature gradient, and the deposit strength or tenacity.

Deposit strength development is related to the physical microstructure of the deposit [Tassopoulos and Rosner 1992]. As individual particles in the deposit increase contacting efficiency with neighboring particles, strength increases significantly [Jagota, Dawson et al. 1988; Jagota and Hui 1990]. Contacting efficiency increases as particles sinter, as vapors condense or liquids accumulate around particles, and as deposits consolidate (smaller particles fill voids around larger particles). These trends have successfully been used to predict some aspects of deposit strength and tenacity development in commercial systems. Sintering, condensation, and consolidation similarly affect deposit tenacity. First-order models of deposit tenacity have been developed based on these concepts in previous work [Baxter 1992; Baxter and Dora 1992; Baxter and Hardesty 1992; Baxter and Hardesty 1992].

Ash Viscosity

Slagging combustors offer the potential advantages of producing an environmentally more benign ash than dry-walled combustors and of increased ash capture and removal in the early stages of the combustion process. Some Combustion 2000 contractors recognize these advantages and are considering slagging combustors as part of their proposed systems. In a slagging combustor, ash viscosity plays the role of the dominant design consideration after the same manner as deposit strength, tenacity and thermal shock resistance do in dry-walled systems. Correlations of deposit viscosity have been proposed by several investigators [Kalmanovitch and Frank 1988; Srinivasachar, Senior et al. 1992] based in large measure on the early work by Urbain [Urbain 1981]. These models are based on relationships and theory from the glass-making industry and represent correlations of viscosity with elemental composition.

Deposit Porosity

Deposit porosity plays a critical role in determining most of the physical and heat transfer properties of the deposit. The development of deposit porosity is influenced by ratio of particle

to condensate in the deposit, the sintering of granules in the deposit, and the generation of gases in fluid material [Raask 1985; Jagota, Dawson et al. 1988; Jagota and Hui 1990]. The results below illustrate direct measurements of porosity and its effect on transport properties such as thermal conductivities. Prediction of such properties is not described in any detail.

Results Illustrating the Impact of Thermal Properties on Boiler Performance

A useful idealization for illustrating the major effects of deposit structure on thermal conductivity is a solid of known porosity and thermal conductivity and with no conduction in the gas phase. Quanta of Vibrational energy (heat) move randomly through this solid. A temperature gradient in the solid is represented by spatial differences in the population of phonons. We seek an expression relating the efficiency at which phonons can move through the porous material to its physical structure. In this simple model, heat transfer proceeds through the solid phase at its customary rate but stops when it encounters the void phase.

Spatial autocorrelation functions relate the probability of two locations being the same phase (solid or void) as a function of distance between them. Generally, autocorrelation functions are bounded by ± 1 and are identically unity at displacements of 0. Characteristically for real materials, they also decay to a limiting values in a smooth but not necessarily monotonic fashion. For isotropic material, the limiting value is the volume fraction of the phase present at a displacement of 0. If the presence of void vs. solid phase is represented as a random event, there are fairly general conditions under which the autocorrelation becomes an exponential decay, with the spatial constant of the exponent a measure of average grain size.

In addition to the amount of solid vs. void volume in the material, the connectedness of the solid phase plays a large role in determining the heat transfer rate. There are higher order correlation functions and connected correlation functions that statistically give clues to the connectedness of a phase. The concept of tortuosity is the approach we have taken, where the tortuosity is defined as the shortest average path length through the solid phase between two points divided by the straight-line distance between the same points. As the solid phase becomes less connected, the tortuosity increases. Using these three most readily available characteristics of the solid phase, the solid volume fraction, the mean particle size, and the tortuosity, we have developed a model for the dependence of the average thermal conductivity on structural properties. We are currently pursuing means of extending the model to anisotropic conditions more sophisticated descriptions of deposit structure. In its current state, the heat transfer model depends on material porosity and tortuosity of both the condensed and gaseous phases, in addition to the thermal conductivity of the two phases.

Aside from the anisotropies of the material, this approach largely ignores the efficiency of the connections between particles. Particles that connect at a single point or over a very small area typically conduct heat far worse than those that are connected over large fractions of their projected areas. In some analyses, the connection points dominate the heat transfer process. This connectedness is captured somewhat, but not entirely, in the concept of the tortuosity. We will examine this aspect of our model in the future. In its current state, it may somewhat over-predict the heat transfer rate in porous media.

The over-prediction is partially compensated by the effect of our initial assumptions. In the original model, the void space was assumed to be non-conducting and radiative heat transfer through the material is ignored. In reality, both intra-media radiative heat transfer and conduction through the gas phase occur. At present, we allow these two simplifications in the model and recognize that they are somewhat balanced by the incomplete descriptions of connectedness of particles in the condensed phase.

In its current state, the heat transfer model reveals some useful insights. These will be illustrated by models of heat transfer through artificially conceived but realistic deposits under boiler-like conditions. The deposits are assumed to exist on cylindrical surfaces and the analysis at this point is limited to one dimension, i.e., the radial dimension.

A one-dimensional, steady state temperature gradient through a cylindrical body with constant transport coefficients is described in this model by

$$T(r) = T_1 - \frac{qr_1}{k_{eff}} \ln\left(\frac{r}{r_1}\right) \quad (100)$$

where the effective thermal conductivity, k_{eff} , is given as a function of the porosity and tortuosity of each of the n phases by

$$k_{eff} = \left(\sum_{s=1}^n \frac{\tau_s}{v_s(1-\xi_s)k_{ss}} \right)^{-1} \quad (101)$$

This form reduces to a linear dependence of deposit temperature on distance in the limit of small deposit thickness relative to the radius of curvature. An example temperature profile is illustrated in Figure 75 for the case of a five-inch deposit resting on a three-inch, outside-diameter steam tube with a 750 K surface temperature exposed to a heat flux of 10 kW/m² and with a thermal conductivity of 2.22 W/(m K). Both the porosity and tortuosity are considered to be unity in the base case, with both parameters being varied by a factor of two to illustrate the effects of deposit properties on the temperature profile. The temperature range depends linearly on the tortuosity and inversely on the porosity such that a change in either quantity changes the difference between deposit surface temperature and tube surface temperature by the same factor. The extent of curvature in the prediction is determined by geometry, not deposit physical properties. Deposits with solid volume fractions lower than (more porous than) 0.5 and tortuosities higher than 2 are common in many systems.

The previous predictions assumed that the incident heat flux, whether from radiation or convection, does not change as deposit surface temperature changes. In practice, incident heat flux is strongly coupled to deposit surface temperature. As an illustration, the heat transfer model predictions for the furnace section of a typical boiler are illustrated below. Only radiative heat transfer is considered, with an assumed black body radiative temperature of 2200 K, deposit thickness of 2 mm, deposit solid phase thermal conductivity of 2.22 W/(m K), and a waterwall composed of 750 K walls made of four inch OD tubes. Predictions of deposit surface

temperature and heat flux are illustrated for a range of porosity and deposit emissivity values. Intra-deposit radiative heat transfer and intra-deposit conductive heat transfer through the gas phase are neglected and deposit tortuosity is assumed to be unity. None of these assumptions is generally accurate. They are made here to allow illustration of the impact of porosity and emissivity on heat transfer.

Figure 75 Parametric variation of deposit temperature as a function of position for various values of the solid volume fraction and tortuosity. See text for details of incident heat flux, etc.

The parametric graph indicated in Figure 76 belies the potential complexity of the relationships between deposit physical properties and heat transfer rates.

Figure 76 Deposit surface temperature and heat flux as a function of porosity and emissivity assuming no intra-deposit radiative heat transfer and a non-conducting gas phase. Tortuosity is assumed to be unity.

While the trends in Figure 76 indicate relatively smoothly varying and monotonic relationships between emissivity or porosity and heat flux, in practice the relationship may not be monotonic. In many cases of practical interest porosity and emissivity are correlated. Heat fluxes under such conditions may not vary monotonically with physical properties. Figure 77 illustrates the trends with an assumed linear relationship between porosity and emissivity, as read by the dual abscissae. As the relationships become more complex, and as factors such as intra-deposit radiative heat transfer and tortuosity are included, the relationships can become increasingly complex.

Figure 77 Deposit surface temperature and heat flux under the same assumptions as in Figure 76 but assuming a linear relationship between emissivity and porosity.

Structural properties of ash vary temporally, effecting changes in both porosity and tortuosity. A common example is sintering or melting of deposits, accompanied by increases in particle-to-particle contacting area and decreases in tortuosity and porosity. A simple example is illustrated in Figure 78. In an idealized case of uniform spheres, a change in linear dimension of less than 15 % is accompanied by a change in contacting efficiency of theoretically zero in the initial case to 50 % in the slightly sintered case. This gives rise to proportional changes in tortuosity and the porosity changes from 0.48 to 0.17. Such changes lend themselves to mathematical treatments in predicting heat transfer through ash deposits. Similar treatments describe the effect of condensation or sulfation on deposit microstructure. These have been used in the past to explain the development of deposit properties ranging from tenacity to strength.

Figure 78 Conceptual illustration of the changes in contacting efficiency and tortuosity with sintering/melting.

In situ, time-resolved, simultaneously measured trends in apparent density and porosity are indicated in Figure 79. The porosity decreases and apparent density increases with time, suggesting that the deposit is sintering. The extent of sintering is quite small, however, with less than a 3% decrease in porosity.

Figure 79 Change in porosity and apparent density with time for an Illinois #6 coal ash accumulating on a tube in cross flow.

Thermal conductivity is determined from measured values of deposit surface temperature, probe temperature, overall heat flux through the probe as determined by change in gas temperature, and deposit thickness. Several measurements of deposit surface temperature and probe surface temperature are made, and since the probe dimensions and material are well characterized, the change in gas temperature can be used without probe surface temperatures to determine the thermal conductivity. In practice, this means there are several avenues available for the determination of thermal conductivity from our data. Results from our current analysis technique are illustrated Figure 80. As is indicated, the thermal conductivity is seen to increase by a factor of about 3 in this case. The data illustrate the dependence of thermal conductivity on porosity/solid fraction, among other things. A complete discussion of these and similar data is included in the Appendix.

Figure 80 Measured and theoretical development of thermal conductivity in an ash deposit formed in the Multifuel Combustor.

Theoretical maxima and minima based on theoretical analyses of deposit properties are illustrated as a function of time for the same data. Over the entire range, they bracket the measured results. These maxima and minima also depend on deposit structure and therefore exhibit time dependencies.

Similar data for a Powder River Basin (Black Thunder) coal are illustrated in Figure 81, illustrating similar trends. Powder River Basin coals produce deposits rich in calcium sulfate. These materials are transparent in the infrared but form as small particulate on the surface, producing a highly reflective deposit with emissivities of approximately 0.2. Biomass ash

deposits formed from calcium sulfate, silica, potassium chloride, and potassium sulfate are qualitatively similar to those from low-rank coals with respect to their optical properties. As seen in the figure, these low rank coals also show indications of sintering.

Figure 81 Measured development of thermal conductivity in an ash deposit from a Black Thunder coal.

Conclusions Regarding Algorithms for Deposit Properties

Ash deposit microstructure influences the mechanical and transport properties by impacting the degree of connectedness between particles and the tortuosity of heat transport through the deposit. Mathematical models are used to predict the impact of microstructural features on bulk deposit properties and on the resulting boiler performance. Deposit surface temperatures can change many hundreds of degrees, depending on deposit thermal and structural properties. Heat fluxes are also dominantly influenced by similar structural properties. Two properties that encapsulate much of the deposit microstructure effect are the porosity and tortuosity. Rational models of the dependence of thermal conductivity on these parameters are presented with predicted results. Experimental examples of how tortuosity and porosity develop in deposits, depending on deposit phase, are also presented.

10. Overall Conclusions

Ash deposit formation has always been and continues to be one of the most important issues impacting design and operation of coal utilization equipment (boilers, gasifiers, etc.) and selection of coals used in such equipment. This Final Report summarizes the principal results of the extensive experimental investigations and the associated theoretical analyses conducted at Sandia's Combustion Research Facility over the past eight years to characterize ash deposit formation during coal combustion and properties of these deposits. Essentially all of the work was conducted in the Multifuel Combustor Laboratory under the sponsorship of the US DOE's Office of Fossil Energy, through the National Energy Technology Laboratory. The principal results and conclusions from our research in the areas of coal characterization, fly ash generation, deposition mechanisms, and deposit properties are summarized, with critical needs assessed. The behavior of inorganic material, during coal combustion is cast in quantitative terms and in a sufficiently fundamental framework, so that it can be applied to a wide range of conditions and coal conversion technologies in order to predict deposit formation as a function of coal properties, boiler design and boiler operation. The principal overall conclusions from this work and critical needs for further research are summarized here under each topic separately.

Coal Characterization

The major means of characterizing inorganic material in coals are briefly summarized. The greatest contribution of this work is the development of a repeatable technique for transforming inorganic elemental information available from standard coal analyses into quantitative, species-specific information about the inorganic materials. This technique is based largely on standardized analyses and the chemical fraction analysis. Chemical fractionation has been used for many years to characterize coals (and other solid fuels, such as biomass), but we are not aware that it has been as systematically analyzed or as fully developed to characterize inorganic species in coals as is done in this document. The primary result of this work is the presentation of a methodology for characterizing the inorganic fractions of coal and other solid fuels, as well as the results from applying this methodology for a wide range of coals. These results provide sufficient detail about coal chemistry to support the remaining tasks. There remain several unresolved issues in this characterization, but in general terms, coal characterization is more advanced than the other tasks and requires less development work. Coal characterization techniques are no longer a critical path item with regard to improving our understanding of the fate of inorganic material during coal combustion. The single critical aspect of characterization of coals, and other fuels such as biomass, needing more research is the establishment of standards with which to compare the various species-specific analyses.

Fly Ash Generation

Fly ash generation focuses on the transformations that occur as coal particles react to form fly ash. In this document, the species indicated from the coal characterization work undergo separate and specific transformations. These are summarized and illustrated for most of the major species that occur in coal. In earlier work, we developed several important mechanisms of fly ash transformation that are used, but not significantly discussed, in this report. These include rates and extents of char fragmentation and mechanisms of inorganic release from reacting coal particles.

There remain several critical issues in describing fly ash transformations. These include specification of thermodynamic and kinetic parameters for the species, descriptions of interactions between species during particle combustion, and description of transport processes limiting such interaction (diffusion coefficients) or resulting from such interactions (viscosity). These issues are discussed, but require additional research for better characterization.

Ash Deposition

The mechanisms and rates of ash deposit formation during coal combustion are discussed in detail. The major mechanisms are summarized and quantitative expressions of their rates are compared. The most important deposition mechanisms are identified and most are accurately characterized. The amount of material deposited by a given mechanism and the influence of that material on deposit properties are both regarded as measures of importance. Less important, but non-negligible deposition mechanisms are also discussed. Agreement and disagreement of several mechanisms with data and theory are highlighted. Resolution of some of the remaining disagreements between various theories and data remains a critical-path issue in understanding the fate of inorganic material in combustors. However, the mechanisms responsible for most deposit mass accumulation during coal combustion are reasonably well characterized.

Deposit Properties

One of the primary focuses of this work in the last several years has been experimental and theoretical analysis of deposit properties. Several major contributions have been made in this regard. For the first time, critical deposit properties such as thermal conductivity, emissivity, strength, etc. have been placed on a firm theoretical foundation. Experimental diagnostics and techniques have been developed for characterizing these properties under realistic combustion conditions. Comparisons of experimental data and theory have resolved some previously confusing results and have led to new disagreements with theory in other areas. Deposit properties remain possibly the single most critical issue to be resolved in describing the fate of inorganic material during combustion.

Final Conclusions

This work has led to new characterization techniques for coals and other solid fuels such as biomass that provide, for the first time, systematic and species-specific information regarding the inorganic material. The transformations of inorganic material during combustion can be described in terms of the net effects of the transformations of these individual species. Deposit formation mechanisms provide a framework for predicting deposition rates for a broad range of particle sizes. Predictions based on these rates many times are quite accurate, although there are important exceptions. A rigorous framework for evaluating deposit properties (thermal conductivity, emissivity, strength, etc.) has been established as a result of this work. Substantial data have been obtained with which to exercise this framework, but this portion of the work is less mature than others. Accurate prediction of deposit properties as functions of coal properties, boiler design, and boiler operating conditions represents the single most critical area where additional research is needed.

11. Acknowledgements

The work summarized here results from the contributions of a large number of students, post doctoral appointees, industrial visitors, colleagues at Sandia National Laboratories, and the sustained support of our sponsors. Additionally, related research contracts with other fuels allowed us to refine experimental or analytical techniques that substantially benefited both projects. I hope that by attempting to identify the major contributors I do not inadvertently forget or offend any of the many people who have contributed. Most of the contributors are indicated below, together with some indication of the nature of their contributions. Some appear twice due to sustained collaborations or multiple functions.

Among these contributors, there are three who have been associated with this work for many years and who deserve particular acknowledgement. Don Hardesty has managed this and most other projects in which I have been involved since I arrived at Sandia. Gian Sclipa has provided deeply appreciated support for this and other projects for many years and is primarily responsible for maintaining the laboratory in a highly productive state. Phil Goldberg has been the contract monitor for this project for many years and has provided sustained guidance and support.

❖ Resident Contributors

- Sandia Managers: Don Hardesty (Department) and Bill McLean (Center)
- Sandia Colleagues: Reggie Mitchell, Tom Fletcher, Judy Wornat, Bob Hurt, Chris Shaddix, Nancy Yang,
- Sandia Technologists: Gian Sclipa, Tim Buteau, Jimmy Ross, Allen Salmi, Andy Gardea, Burt Brown
- Post Doctoral Appointees: Steve Buckley, Allen Robinson, Melissa Lunden, Marc Rumminger, Terttaliisa Lind, Geoff German
- Professors: Bryan Jenkins, Peter Bernath, Ziad Habib
- Industrial Visitors: Helle Junker, Scott Turn, Stan Harding, Aniefiok Akanatuk, Javier Ballester, Markku Orjala, Terttaliisa Lind
- High School Teachers: Steve Giles, Lisa Ryder, Linda Slogan
- Ph.D. Students: Hanne Nielsen, Scott Sinuefield, Helle Junker, Ted Mao, Søren Kær, Jaimee Dong, Galen Richards, Thomas Linsmeyer, Hanspeter Kaufman, Tom Gale, Reyhaneh Shenassa
- Undergraduate Students: Gretchen Streiter, Andrew Peronto, Candace Morey, April Brough, Hobart Lee, Jordan Brough, Hanne Lee, Judy Gilmer, Peter Adams, Alex Villa, Ed Muzio, Alex Saporito, Keith Casavant

❖ Non-resident Contributors

- Sponsors: Philip Goldberg, Arun Mehta, Ray Costello, Valri Robinson
- Industrial Professionals: Dick Bryers, Dick Borio
- Professors: Honghi Tran, Jim Frederick, Bryan Jenkins
- Industrial Professionals: Tom Miles, Rick Wessel, Jørn Roed, Richard DeSollar, Bob Roscoe, Martha Rollins, Doug Boylan, Jim Chaney, Bill Carlson, Randy Bates

12. References

- Abbott, M. F., R. E. Douglas, et al. (1993). A Modeling Strategy for Correlating Coal Quality to Power Plant Performance and Power Costs. Engineering Foundation Conference on The Impact of Ash Deposition on Coal-Fired Plants, Solihull, England.
- Abryutin, A. A. and E. S. Karasina (1970). "Thermal conductivity and thermal resistance of ash deposits in boiler furnaces." Teploenergetika (Thermal Engineering) 17(12): 46-50.
- Anderson, D. W., R. Viskanta, et al. (1987). "Effective Thermal Conductivity of Coal Ash Deposits at Moderate to High Temperatures." Journal of Engineering for Gas Turbines and Power 109: 215-221.
- Batchelor, G. K. (1949). "Diffusion in a Field of Homogeneous Turbulence." Australian Journal of Scientific Research A2: 437.
- Batchelor, G. K. (1957). "Diffusion in Free Turbulent Shear Flows." Journal of Fluid Mechanics 3: 67.
- Baxter, L. L. (1989). Turbulent Transport of Particles, Brigham Young University.
- Baxter, L. L. (1990). Ash Composition Prediction as a Function of Coal Type, Operating Conditions, and Boiler Location. EPRI conference on the Effects of Coal Quality on Power Plants, St. Louis, Missouri, Electric Power Research Institute.
- Baxter, L. L. (1990). "The Evolution of Mineral Particle Size Distributions During Early Stages of Coal Combustion." Progress in Energy and Combustion Sciences 16: 261-266.
- Baxter, L. L. (1992). Boiler Performance with Blends of Eastern and Western Coals. EPRI Conference on The Effects of Coal Quality on Power Plants, San Diego, CA.
- Baxter, L. L. (1992). "Char Fragmentation and Fly Ash Formation During Pulverized Coal Combustion." Combustion and Flame 90: 174-184.
- Baxter, L. L. (1993). "Ash Deposition During Biomass and Coal Combustion : a Mechanistic Approach." Biomass & Bioenergy 4(#2): 85-102.
- Baxter, L. L. (1993). "Ash Deposition During Biomass and Coal Combustion: A Mechanistic Approach." Biomass and Bioenergy 4(2): 85-102.
- Baxter, L. L. (1993). In Situ, Real-Time Emission FTIR Spectroscopy as a Diagnostic for Ash Deposition During Coal Combustion. Engineering Foundation Conference on The Impact of Ash Deposition on Coal-Fired Plants, Solihull, England.
- Baxter, L. L. (1998). "Influence of Ash Deposit Chemistry and Structure On Physical and Transport-Properties." Fuel Processing Technology 56(#1-2): 81-88.
- Baxter, L. L., M. F. Abbott, et al. (1991). Dependence of Elemental Ash Deposit Composition on Coal Ash Chemistry and Combustor Environment. Engineering Foundation Conference on Inorganic Transformations and Ash Deposition During Combustion, Palm Coast, Florida, The American Society of Mechanical Engineers.
- Baxter, L. L., M. Blander, et al. (1997). Thermochemical Equilibrium as an Indicator of Ash Deposition Problems in Biomass Boilers. Developments in Thermochemical Biomass Conversion. A. V. Bridgwater and D. G. B. Boocock. London, Blackie Academic & Professional. 2: 1278-1292.
- Baxter, L. L. and N. Chigier, Eds. (1996). Advanced Technology Applications to Ash-Related Problems in Boilers. New York, Elsevier.

- Baxter, L. L. and R. W. DeSollar (1991). Ash Deposition as a Function of Coal Type, Location in a Boiler, and Boiler Operating Conditions: Predictions Compared to Observations. International Conference on Environmental Control of Combustion Processes, Honolulu, HA.
- Baxter, L. L. and R. W. DeSollar (1993). "A Mechanistic Description of Ash Deposition During Pulverized Coal Combustion: Predictions Compared to Observations." Fuel 72(10): 1411-1418.
- Baxter, L. L. and L. Dora (1992). "The Combustion Behavior of a Blend of Eastern and Western Coals: Comparisons Between a Blend and Its Individual Components." ASME Paper No. 92-JPGC-FACT-14.
- Baxter, L. L., T. H. Fletcher, et al. (1988). "Spectral Emittance Measurements of Coal Particles." Energy & Fuels 2(#4): 423-430.
- Baxter, L. L., T. Gale, et al. (1997). Influence of Ash Deposit Chemistry and Structure on Physical and Transport Properties. Developments in Thermochemical Biomass Conversion. A. V. Bridgwater and D. G. B. Boocock. London, Blackie Academic and Professional. 2: 1247-1262.
- Baxter, L. L. and D. R. Hardesty (1990). The Fate of Mineral Matter During Pulverized Coal Combustion, Sandia National Laboratories.
- Baxter, L. L. and D. R. Hardesty (1992). The Fate of Mineral Matter During Pulverized Coal Combustion: April - June, Sandia National Laboratories.
- Baxter, L. L. and D. R. Hardesty (1992). The Fate of Mineral Matter During Pulverized Coal Combustion: January-March, Sandia National Laboratories.
- Baxter, L. L., K. R. Hencken, et al. (1990). The Dynamic Variation of Particle Capture Efficiency During Ash Deposition in Coal-Coal Fired Combustors. Twenty-Third Symposium (International) on Combustion, Orleans, France.
- Baxter, L. L. and B. M. Jenkins (1995). Laboratory Illustrations of the Transformations and Deposition of Inorganic Material in Biomass Boilers. ACS National Meeting, Division of Fuel Chemistry, Chicago, IL.
- Baxter, L. L., B. M. Jenkins, et al. (1996). Inorganic Material Deposition in Biomass Boilers. 9th European Bioenergy Conference, Copenhagen, Denmark, Elsevier.
- Baxter, L. L., B. M. Jenkins, et al. (1995). Ash Behavior in Biomass Boilers.
- Baxter, L. L., T. R. Miles, et al. (1996). The Behavior of Inorganic Material in Biomass-Fired Power Boilers: Field and Laboratory Experiences. Engineering Foundation Conference on Industrial and Utility Use of Biomass, Snowbird, UT.
- Baxter, L. L., T. R. Miles, et al. (1997). The Behavior of Inorganic Material in Biomass-Fired Power Boilers: An Overview of the Alkali Deposits Project. Developments in Thermochemical Biomass Conversion. A. V. Bridgwater and D. G. B. Boocock. London, Blackie Academic & Professional. 2: 1424-1444.
- Baxter, L. L., T. R. Miles, et al. (1993). Transformations and Deposition of Inorganic Material in Biomass Boilers. Second International Conference on Combustion Technologies for a Clean Environment, Lisbon, Portugal, Commission of European Communities.
- Baxter, L. L., R. E. Mitchell, et al. (1997). "Release of Inorganic Material During Coal Devolatilization." Combustion and Flame 108(#4): 494-502.
- Baxter, L. L. and H. P. Nielsen (1997). The Effects of Fuel-bound Chlorine and Alkali on Corrosion Initiation. American Chemical Society Annual Meeting, Las Vegas, NV.

- Baxter, L. L., G. H. Richards, et al. (1993). "In-Situ ; Real-Time Characterization of Coal Ash Deposits Using Fourier-Transform Infrared-Emission Spectroscopy." Energy & Fuels 7(#6): 755-760.
- Baxter, L. L., A. L. Robinson, et al. (1997). Biomass-Coal Cofiring: Imperatives and Experimental Investigations. 3rd Biomass Conference of the Americas, Montréal, Ontario, Canada.
- Beer, J. M. and N. A. Chigier (1983). Combustion Aerodynamics. Melbourne, Florida, Krieger.
- Beér, J. M., L. S. Monroe, et al. (1990). From Coal Mineral Matter Properties to Fly Ash Deposition Tendencies: a Modeling Approach. The Seventh International Pittsburgh Coal Conference, Pittsburgh, PA.
- Benson, S. A., J. P. Hurley, et al. (1993). "Predicting ash behavior in utility boilers." Energy & Fuels 7: 746-754.
- Benson, S. A., E. N. Steadman, et al. (1990). In Situ Determination of Temperature Distributions in Ash Deposits in a Pilot Scale Furnace. Mineral Matter and Ash Deposition From Coal. R. W. Bryers and K. S. Vorres, Engineering Foundation Conferences, United Engineering Trustees, Inc.: 423-434.
- Bird, R. B., W. E. Stewart, et al. (1960). Transport Phenomena. New York, Wiley.
- Bohren, C. F. and D. R. Huffman (1983). Absorption and Scattering of Light by Small Particles. New York, John Wiley & Sons.
- Boni, A. A., J. M. Beér, et al. (1990). Transformations of Inorganic Coal Constituents in Combustion Systems.
- Boni, A. A., S. A. Johnson, et al. (1990). Mineral Matter Transformations During Coal Combustion: Fundamental Results and Relevance to Deposition. ASME Seminar on Fireside Fouling Problems, Provo, Utah.
- Boow, J. and P. R. Goard (1969). "Fireside deposits and their effect on heat transfer in a pulverized-fuel-fired boiler: Part III. The influence of the physical characteristics of the deposit on its radiant emittance and effective thermal conductance." Journal of the Institute of Fuel 42: 412-419.
- Borio, R. W. and A. A. Levasseur (1991). Predicting the Effects of Ash Deposition on Boiler Performance: Where Do We Stand? Eighth Annual International Pittsburgh Coal Conference, Pittsburgh, PA, The University of Pittsburgh.
- Bouris, D. and G. Bergeles (1996). "Particle-surface interactions in heat exchanger fouling." Transactions of the ASME Journal of Fluids Engineering 118: 574-581.
- Bouris, D. and G. Bergeles (1997). "Numerical calculation of the effect of deposit formation on heat-exchanger efficiency." International Journal of Heat and Mass Transfer 40(#17): 4073-4084.
- Brekke, D. W., C. J. Zygarlicke, et al. (1991). Practical Application of Advanced Coal Analysis to Coal Blending. Eighth Annual Pittsburgh Coal Conference, Pittsburgh, PA, The University of Pittsburgh.
- Brun, E., J. Lerous, et al. (1955). J. Rech. Centre Nat. Rech. Scient. 31: 256.
- Byers, R. L. and S. Calvert (1969). "Particle Deposition from Turbulent Streams by Means of Thermal Force." Industrial and Engineering Chemistry Fundamentals 8(4): 646-655.
- Canavos, G. C. (1984). Applied probability and statistical methods. Boston, Little, Brown and Company.

- Carter, H. R. and C. G. Koksai (1991). On-line Imaging and Emissivity Measurements to Determine Furnace Cleanliness. International Joint Power Generation Conference, San Diego, CA.
- Carter, H. R., C. G. Koksai, et al. (1992). Furnace Cleaning in Utility Boilers Burning Powder River Basin Coals, ASME.
- Castillo, J. L. and D. E. Rosner (1988). "A Nonequilibrium Theory of Surface Deposition from Particle-Laden, Dilute, Condensable Vapor-Containing, Laminar Boundary Layers." International Journal of Multiphase Flow **14**: 99-120.
- Castillo, J. L., D. W. Mackowski, et al. (1990). "Photophoretic Modification of the Transport of Absorbing Particles Across Combustion Gas Boundary Layers." Progress in Energy and Combustion Science **16**: 253-260.
- Cawood, W. (1936). Transactions of the Faraday Society **32**: 1068.
- Charon, O., A. F. Sarofim, et al. (1990). "Distribution of Mineral Matter in Pulverized Coal." Progress in Energy and Combustion Science **16**: 319-326.
- Chen, J. C. and S. Niksa (1992). "Coal Devolatilization during Rapid Transient Heating 1. Primary Devolatilization." Energy & Fuels **6**(3): 254-264.
- Chen, J. C. and S. Niksa (1992). Suppressed Nitrogen Evolution from Coal-Derived Soot and Low-Volatility Chars. Twenty-Fourth Symposium (International) on Combustion, Sydney, Australia, The Combustion Institute.
- Chigier, N. A. (1976). "The Atomization and Burning of Liquid Fuel Sprays." Progress in Energy and Combustion Science **2**: 97.
- Chow, O. K. and F. F. Lexa (1987). Combustion Characterization of the Kentucky No. 9 Cleaned Coals, Electric Power Research Institute.
- Couch, G. (1994). Understanding slagging and fouling in pf combustion, IEA Coal Research.
- Crowe, C. T. (1979). Gas-Particle Flow. Pulverized Coal Combustion and Gasification. L. D. Smoot and D. D. Pratt. New York, Plenum: 15-56.
- Crowe, C. T. (1982). "Review - Numerical Models for Dilute Gas-Particle Flows." Transactions of ASME, Journal of Fluids Engineering **104**: 197.
- Csanady, G. T. (1973). Turbulent Diffusion in the Environment. Dordrecht, Holland, D. Reidel Publishing Company.
- Durant, J. F., A. F. Kwasnik, et al. (1989). Impacts of Cleaning Texas Lignite on "Boiler Performance and Economics, Electric Power Research Institute.
- Einstein, A. (1954). Zeitschrift der Physik **27**: 1.
- Ethier, S. N. and T. G. Kurtz (1986). Markov Processes. New York, Wiley.
- Faeth, G. M. (1983). "Evaporation and Combustion of Sprays." Progress in Energy and Combustion Science **9**: 1-.
- Fletcher, T. H. (1989). "Time-Resolved Particle Temperature and Mass Loss Measurements of a Bituminous Coal During Devolatilization." Combustion and Flame **78**: 223-236.
- Friedlander, S. K. (1977). Smoke, Dust, and Haze. New York, Wiley.
- Friedlander, S. K. and H. F. Johnstone (1957). "Deposition of Suspended Particles from Turbulent Gas Streams." Industrial and Engineering Chemistry **49**: 1151-1156.
- Fuchs, N. A. (1964). The Mechanics of Aerosols. New York, Dover.
- Galbreath, K., C. Zygarlicke, et al. (1996). "Collaborative study of quantitative coal mineral analysis using computer-controlled scanning electron microscopy." Fuel **75**(4): 424-430.

- Gardiner, C. W. (1985). Handbook of Stochastic Methods for Physics, Chemistry, and the Natural Sciences. Berlin, Springer-Verlag.
- Gavalas, G. R. (1980). AIChE Journal **26**: 577.
- Goetz, F. J., N. Y. Nsakala, et al. (1979). "Development of Method for Determining Emissivities and Absorptivities of Coal Ash Deposits." Journal of Engineering for Power **101**: 607-621.
- Gökoglu, S. A. and D. E. Rosner (1984). "Correlation of Thermophoretically-Modified Small Particle Diffusional Deposition Rates in Forced Convection Systems with Variable Properties, Transpiration Cooling and/or Viscous Dissipation." International Journal of Heat and Mass Transfer **27**: 639-646.
- Gökoglu, S. A. and D. E. Rosner (1985). "Thermophoretically Enhanced Mass Transport Rates to Solid and Transpiration-Cooled Walls Across Turbulent (Law-of-the-Wall) Boundary Layers." Industrial and Engineering Chemistry Fundamentals **24**: 208-214.
- Gökoglu, S. A. and D. E. Rosner (1986). "Thermophoretically Augmented Mass Transfer Rates to Solid Walls Across Laminar Boundary Layers." AIAA Journal **24**: 172-179.
- Goldschmidt, V. W., M. K. Householder, et al. (1972). "Turbulent Diffusion of Small Particles." Progress in Heat and Mass Transfer **6**: 487.
- Golovin, V. N. (1964). "Investigation of tube fouling in a TP-90 boiler." Teploenergetika **11**(3): 23-28.
- Goodwin, D. G. (1986). Infrared Optical Constants of Coal Slags, Stanford University.
- Gosman, A. D. and E. Ioannides (1981). Aspects of Computer Simulations of Liquid-Fueled Combustion, AIAA.
- Griffith, B. F., F. G. Lexa, et al. (1988). Pilot-Scale Combustion Characterization of Two Illinois Coals, Electric Power Research Institute.
- Gupta, R., T. F. Wall, et al. (1997). Thermal Conductivity of Coal Ash Deposits. Engineering Foundation Conference on the Impact of Mineral Impurities on Solid Fuel Combustion, Kona, HI, Plenum Press.
- Harding, N. S. and M. C. Mai (1990). Elemental Partitioning during Pilot-Scale Combustion Tests — Effects on Ash Deposit Composition. Mineral Matter and Ash Deposition from Coal. R. W. Bryers and K. S. Vorres, Engineering Trustees, Inc.: 375-399.
- Helble, J. J., M. Neville, et al. (1986). Aggregate Formation from Vaporized Ash During Pulverized Coal Combustion. Twenty-First Symposium (International) on Combustion, Technical University of Munich, Germany, The Combustion Institute.
- Hettner, G. (1926). Zeitschrift der Physik **37**: 179.
- Hinze, J. O. (1975). Turbulence. New York, McGraw-Hill.
- Huffman, G. P., F. E. Huggins, et al. (1989). "Investigation of the transformations of pyrite in a drop-tube furnace." Fuel **68**(4): 485-490.
- Huggins, F. E., D. A. Kosmack, et al. (1980). Scanning Electron Microscopy **1**: 531.
- Im, K. H. and P. M. Chung (1983). "Particulate Deposition from Turbulent Parallel Streams." AIChE Journal **29**(3): 498-505.
- Israel, R. and D. E. Rosner (1983). "Use of a Generalized Stokes Number to Determine the Aerodynamic Capture Efficiency of Non-Stokesian Particles from a Compressible Gas Flow." Aerosol Science and Technology **2**: 45-51.
- Jacobsen, S. and J. R. Brock (1965). "The Thermal Force on Spherical Sodium Chloride Aerosols." Journal of Colloid Science **20**: 544-554.

- Jagota, A., P. R. Dawson, et al. (1988). "An Anisotropic Continuum Model for the Sintering and Compaction of Powder Packings." Mechanics of Materials **11**: 357-372.
- Jagota, A. and C. Y. Hui (1990). "The Effective Thermal Conductivity of a Packing of Spheres." Transactions of the ASME, Journal of Applied Mechanics **57**: 789-791.
- Kalinske, A. A. and C. L. Pien (1944). "Eddy Diffusion." Industrial and Engineering Chemistry **36**: 220.
- Kalmanovitch, D. P. and M. Frank (1988). An Effective Model of Viscosity for Ash Deposition Phenomena. Mineral Matter and Ash Deposition from Coal, Santa Barbara, CA, The Engineering Foundation.
- Kuo, K. K. (1986). Principles of Combustion. New York, Wiley.
- Laitone, J. A. (1981). "A Numerical Solution for Gas-Particle Flows at High Reynolds Numbers." Journal of Applied Mechanics **48**: 465-471.
- Laurendeau, N. M. (1978). "Heterogeneous Kinetics of Coal Char Gasification and Combustion." Progress in Energy and Combustion Science **4**: 221-270.
- Lee, F. C. C. and F. C. Lockwood (1999). "Modelling ash deposition in pulverized coal-fired applications." Progress in Energy and Combustion Science **25**(#2): 117-132.
- Lilly, G. P. (1973). "Effect of Particle Size on Particle Eddy Diffusivity." Industrial and Engineering Chemistry, Fundamentals **12**: 268.
- Loehden, D., P. M. Walsh, et al. (1989). "Generation and Deposition of Fly Ash in the Combustion of Pulverised Coal." Journal of the Institute of Energy **62**: 119-127.
- Markham, J. R., P. E. Best, et al. (1992). "Measurement of Radiative Properties of Ash and Slag by FT-IR Emission and Reflection Spectroscopy." Transactions of the ASME **114**: 458-464.
- Miller, R. N. and P. H. Given (1978). A Geochemical Study of the Inorganic Constituents in Some Low-Rank Coals, U.S. DOE.
- Mills, K. C. and J. M. Rhine (1989). "The measurement and estimation of the physical properties of slags formed during coal gasification 2. Properties relevant to heat transfer." Fuel **68**: 904-910.
- Mitchell, R. E. (1987). "Experimentally Determined Overall Burning Rates of Coal Chars." Combustion Science and Technology **53**: 165-186.
- Mitor, V. V. and I. N. Konopel'Ko (1966). "The Study of Emissivity of Solid Bodies." Thermal Engineering **13**(7): 92-97.
- Mitor, V. V. and I. N. Konopel'Ko (1970). "Experimental Investigation of Radiation and Reflection Characteristics of Some Solid Bodies." Thermal Engineering **16**(5): 47-52.
- Mitor, V. V. and I. N. Konopel'Ko (1970). "A Study of the Emissivity Factor of Ash Deposits and Certain Refractory Materials." Thermal Engineering **17**(19): 61-63.
- Mulcahy, M. F. R., J. Boow, et al. (1966). "Fireside Deposits and their Effect on Heat Transfer in a Pulverized-fuel-fired Boiler. Part I: The Radiant Emittance and Effective Thermal Conductance of the Deposits." Journal of the Institute of Fuel **39**: 385-394.
- Mulcahy, M. F. R., J. Boow, et al. (1966). "Fireside Deposits and their Effect on Heat Transfer in a Pulverized-fuel-fired Boiler. Part II: The Effect of the Deposit on heat Transfer from the Combustion Chamber Considered as a Continuous Well-stirred Reactor." Journal of the Institute of Fuel **39**: 394-398.
- Papoulis, A. (1984). Probability, Random Variables, and Stochastic Processes. New York, McGraw-Hill.

- Raask, E. (1984). "Creation, capture and coalescence of coal species in coal flames." Journal of the Institute of Energy **57**: 231.
- Raask, E. (1985). Mineral impurities in coal combustion: Behavior, problems, and remedial measures. Washington, Hemisphere Publishing Corporation.
- Ramer, E. R. and D. V. Martello (1996). Characterization of ash deposit structure from planar sections: Results and challenges. Applications of advanced technology to ash-related problems in boilers. L. L. Baxter and R. DeSollar. New York, Plenum Press: 309-323.
- Richards, G. A., R. G. Logan, et al. (1992). "Ash deposition at coal-fired gas turbine conditions: Surface and combustion temperature effects." Transaction of the ASME Journal of Engineering for Gas Turbines and Power **114**: 132-138.
- Richards, G. H., P. N. Slater, et al. (1993). "Simulation of Ash Deposit Growth in a Pulverized Coal-Fired Pilot-Scale Reactor." Energy & Fuels **7**(#6): 774-781.
- Robinson, A., L. L. Baxter, et al. (1998). Issues Associated with Coal-Biomass Cofiring. Bioenergy '98, Madison, Wisconsin.
- Robinson, A. L., S. G. Buckley, et al. (1998). In Situ Measurements of the Thermal Conductivity of Ash Deposits. Twenty-Seventh Symposium (International) on Combustion, Boulder, CO, Combustion Institute.
- Robinson, A. L., S. G. Buckley, et al. (2000). "Thermal Conductivity of Ash Deposits 1: Measurement Technique." Energy & Fuels: submitted.
- Robinson, A. L., S. G. Buckley, et al. (1997). In Situ Measurements of the Thermal Conductivity of Ash Deposits formed in a Pilot-Scale Combustor. Engineering Foundation Conference on the Impact of Mineral Impurities on Solid Fuel Combustion, Kona, HI.
- Robinson, A. L., S. G. Buckley, et al. (2000). "Thermal Conductivity of Ash Deposits 2: Effects of Sintering." Energy & Fuels: submitted.
- Robinson, A. L., H. Junker, et al. (1998). Interactions between Coal and Biomass when Cofiring. Twenty-Seventh Symposium (International) on Combustion, Boulder, CO, Combustion Institute.
- Rosner, D. E. (1989). "Total Mass Deposition Rates from "Polydispersed" Aerosols." AIChE Journal **35**(1): 164-167.
- Rosner, D. E. and R. Nagarajan (1985). "Transport-Induced Shifts in Condensate Dewpoint and Composition in Multicomponent Systems with Chemical Reaction." Chemical Engineering Science **40**(2): 177-186.
- Rosner, D. E. and M. Tassopoulos (1989). "Deposition Rates from Polydispersed Particle Populations of Arbitrary Spread." AIChE Journal **35**(9): 1497-1508.
- Schlichting, H. (1979). Boundary-Layer Theory. New York, McGraw-Hill.
- Senior, C. L. (1997). "Predicting removal of coal ash deposits in convective heat exchangers." Energy & Fuels **11**(#2): 416-420.
- Serio, M. A., D. G. Hamblen, et al. (1987). "Kinetics of Volatile Product Evolution in Coal Pyrolysis: Experiment and Theory." Energy & Fuels **1**: 138-152.
- Shah, H., G. P. Huffman, et al. (1991). Graphical Representation of CCSEM Data for Coal Minerals and Ash Particles. Seminar on Fireside Fouling Problems, Brigham Young University, Provo, UT, Advanced Combustion Engineering Research Center.
- Shuen, J.-S., L.-D. Chen, et al. (1983). "Evaluation of a Stochastic Model of Particle Dispersion in a Turbulent Round Jet." AIChE Journal **29**: 167.

- Sinquefield, S. A., L. L. Baxter, et al. (1998). An Experimental Study of the Mechanisms of Fine Particle Deposition in Kraft Recovery Boilers. 1998 TAPPI International Chemical Recovery Conference, Tampa, FL, TAPPI Press.
- Smouse, S. M. and C. L. Wagoner (1991). Deposit Initiation: Part 2 — Experimental Verification of Hypothesis Using a Simulated Superheater Tube. Conference on Inorganic Transformations and Ash Deposition During Combustion, Palm Coast, Florida, ASME.
- Snyder, W. H. and J. L. Lumley (1971). "Some Measurements of Particle Velocity Autocorrelation Functions in a Turbulent Flow." Journal of Fluid Mechanics **48**: 41-71.
- Srinivasachar, S. and A. A. Boni (1989). "A kinetic model for pyrite transformations in a combustion environment." Fuel **68**(7): 829-836.
- Srinivasachar, S., J. J. Helble, et al. (1990). An Experimental Study of the Inertial Deposition of Ash Under Coal Combustion Conditions. Twenty-Third Symposium (International) on Combustion, The University of Orléans, Orléans, France, The Combustion Institute.
- Srinivasachar, S., J. J. Helble, et al. (1990). "Mineral Behavior During Coal Combustion 1. Pyrite Transformations." Progress in Energy and Combustion Science **16**: 281-292.
- Srinivasachar, S., J. J. Helble, et al. (1991). An experimental study of the inertial deposition of ash under coal combustion conditions. Proceedings of the Twenty-Third Symposium on Combustion, The Combustion Institute.
- Srinivasachar, S., J. J. Helble, et al. (1990). "Mineral Behavior During Coal Combustion 2. Illite Transformations." Progress in Energy and Combustion Science **16**: 293-302.
- Srinivasachar, S., J. J. Helble, et al. (1990). "A Kinetic Description of Vapor Phase Alkali Transformations in Combustion Systems." Progress in Energy and Combustion Science **16**: 303-309.
- Srinivasachar, S., C. L. Senior, et al. (1992). A Fundamental Approach to the Prediction of Coal Ash Deposit Formation in Combustion Systems. The Twenty-Fourth Symposium (International) on Combustion, The University of Sydney, Australia, The Combustion Institute.
- Street, P. J. and C. S. Twamley (1971). "Fuel Particle Emissivities." Journal of the Institute of Fuel **44**: 477-478.
- Sunden, B. (1980). "Conjugate heat transfer from circular cylinders in low reynolds number flow." International Journal of Heat and Mass Transfer **23**: 1359-1367.
- Tassopoulos, M., J. A. O'Brien, et al. (1989). "Simulation of Microstructure/Mechanism Relationships in Particle Deposition." AIChE Journal **35**(6): 967-980.
- Tassopoulos, M. and D. Rosner (1992). "Simulation of Vapor Diffusion in Anisotropic Particulate Deposits." Chemical Engineering Science **47**(2): 421-443.
- Tassopoulos, M. and D. E. Rosner (1992). "The Effective Thermal Conductivity of Packings of Spheres I. Conduction through the Solid Phase." International Journal of Heat and Mass Transfer.
- Tassopoulos, M. and D. E. Rosner (1992). "The Effective Thermal Conductivity of Packings of Spheres II. Conduction through the Solid and Void Spaces." International Journal of Heat and Mass Transfer.
- Tassopoulos, M. and D. E. Rosner (1992). "Microstructural Descriptors Characterizing Granular Deposits." AIChE Journal **38**(1): 15-25.
- Taylor, G. I. (1921). "Diffusion by Continuous Movements." Proceedings of the London Mathematical Society **20**: 196-211.

- Taylor, G. I. (1932). "The Transport of Vorticity and Heat through Fluids in Turbulent Motion." Proceedings of the Royal Society of London **135**(A): 685-706.
- Taylor, G. I. (1935). "Statistical Theory of Turbulence." Proceedings of the Royal Society of London **A 151**: 421-464.
- Taylor, G. I. (1938). "The Spectrum of Turbulence." Proceedings of the Royal Society of London **A 164**: 476.
- Torquato, S. (1992). Connection Between Morphology and Effective Properties of Heterogeneous Materials. The Winter Annual Meeting of the American Society of Mechanical Engineers, Anaheim, California, American Society of Mechanical Engineers.
- Touloukian, Y. S. and C. J. Ho, Eds. (1989). Thermal Radiative Properties of Nonmetallic Solids. New York, Plenum.
- Ubhayakar, S. K., D. B. Stickler, et al. (1976). Rapid Devolatilization of Pulverized Coal in Hot Combustion Gases. Sixteenth Symposium (International) on Combustion, Massachusetts Institute of Technology, Cambridge, MA, The Combustion Institute.
- Urbain, G. (1981). "Viscosity of Silicate Melts." Journal of the British Ceramic Society **80**.
- Vassallo, A. M., P. A. Cole-Clarke, et al. (1992). "Infrared Emission Spectroscopy of Coal Minerals and their Thermal Transformations." Applied Spectroscopy **46**(1): 73-78.
- Vassallo, A. M. and K. S. Finnie (1992). "Infrared Emission Spectroscopy of Some Sulfate Minerals." Applied Spectroscopy **46**: 1477-1482.
- Wagoner, C. L. and X.-X. Yan (1991). Deposit Initiation via Thermophoresis: Part 1 — Insight on Deceleration and Retention of Inertially-transported particles. Conference on Inorganic Transformations and Ash Deposition During Combustion, Palm Coast, Florida, ASME.
- Wall, T. F., S. P. Bhattacharya, et al. (1995). "The Character of Ash Deposits and the Thermal Performance of Furnaces." Fuel Processing Technology **44**(#1-3): 143-153.
- Wall, T. F., S. P. Bhattacharya, et al. (1994). The Properties and Thermal Effects of Ash Deposits in Coal-Fired Furnaces. The Impact of Ash Deposition on Coal-Fired Plants. J. Williamson and F. Wigely. Washington, D.C., Taylor & Francis: 463-477.
- Walsh, P. M., A. F. Sarofim, et al. (1992). "Fouling of convective heat exchangers by lignitic coal ash." Energy & Fuels **6**: 709-715.
- Walsh, P. M., A. N. Sayre, et al. (1990). "Deposition of Bituminous Coal Ash on an Isolated Heat Exchanger Tube: Effects of Coal Properties on Deposit Growth." Progress in Energy and Combustion Science **16**: 327-346.
- Wang, H. F. and J. N. Harb (1997). "Modeling of ash deposition in large-scale combustion facilities burning pulverized coal." Progress in Energy and Combustion Science **23**(#3): 267-282.
- Ziesmer, B. C., L. J. Barna, et al. (1990). A Utility Perspective on Western Coals — Operating Experience and Methods for Screening Potential Fuel Supplies. Effects of Coal Quality on Power Plants — Second International Conference, Saint Louis, Missouri, Electric Power Research Institute.
- Zygarlicke, C. J., D. P. McCollor, et al. (1992). Combustion Inorganic Transformations, University of North Dakota Energy and Environmental Research Center.
- Zygarlicke, C. J., M. Ramanathan, et al. (1992). Fly Ash Particle-Size Distribution and Composition: Experimental and Phenomenological Approach. Inorganic Transformations and Ash Deposition During Combustion. S. A. Benson. New York, American Society of Mechanical Engineers: 525-544.

Appendix 1: Coal Characterization

Summary of Analysis Procedures

The American Society for Testing and Materials (ASTM) Committee on Coal and Coke (Committee D05) has responsibility for most of the standardized tests commonly used for coal analysis within the US. The scope of the Committee is (1) promotion and dissemination of research and knowledge and (2) development of standards for coal and coke derived from coal. Standards include terminology, classifications on the basis of chemical and physical characteristics, guides, practices and test methods for the samplings of coal and coke derived from coal as well as the analysis of the chemical and physical characteristics of coal and coke derived from coal. Most of the standards of concern to this project fall under one of two subcommittees: Methods of Analysis Subcommittee (D05.21) or the Major Elements in Ash and Trace Elements of Coal Subcommittee (D05.29).

Table 12 Coal-related standards published standards under the jurisdiction of the Methods of Analysis Subcommittee (D05.21) of the ASTM.

Standard No.	Title
D1412-99	Standard Test Method for Equilibrium Moisture of Coal at 96 to 97 Percent Relative Humidity and 30°C
D1756-96	Standard Test Method for Determination as Carbon Dioxide of Carbonate Carbon in Coal
D1857-87(1994)	Standard Test Method for Fusibility of Coal and Coke Ash
D1989-97	Standard Test Method for Gross Calorific Value of Coal and Coke by Microprocessor Controlled Isoperibol Calorimeters
D2015-96	Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter
D2361-95	Standard Test Method for Chlorine in Coal
D2492-90(1998)	Standard Test Method for Forms of Sulfur in Coal
D2961-95a	Standard Test Method for Total Moisture in Coal Reduced to 2.36-mm (No. 8) Mesh Top Sieve Size (Limited-Purpose Method)
D3172-89(1997)	Standard Practice for Proximate Analysis of Coal and Coke
D3173-87(1996)	Standard Test Method for Moisture in the Analysis Sample of Coal and Coke
D3174-97e1	Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal
D3175-89a(1997)	Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke
D3176-89	Standard Practice for Ultimate Analysis of Coal and Coke
D3177-89(1997)	Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke
D3178-89	Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke
D3179-89(1997)	Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke
D3180-89(1997)	Standard Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
D3286-96	Standard Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter
D3302-99	Standard Test Method for Total Moisture in Coal
D4208-88(1997)	Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method
D4239-97e1	Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods
D5142-90(1998)	Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures
D5373-93(1997)	Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke
D5865-99a	Standard Test Method for Gross Calorific Value of Coal and Coke

Table 13 Coal-related standards published standards under the jurisdiction of the Major Elements in Ash and Trace Elements of Coal Subcommittee (D05.29) of the ASTM.

Standard No.	Title
D1757-96	Standard Test Method for Sulfur in Ash from Coal and Coke
D2795-86(1991)e1	Standard Test Methods for Analysis of Coal and Coke Ash
D3682-96	Standard Test Method for Major and Minor Elements in Coal and Coke Ash by Atomic Absorption
D3683-94	Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption
D3684-94	Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method
D3761-96	Standard Test Method for Total Fluorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method
D4326-97	Standard Test Method for Major and Minor Elements in Coal and Coke Ash By X-Ray Fluorescence
D4606-95	Standard Test Method for Determination of Arsenic and Selenium in Coal by the Hydride Generation/Atomic Absorption Method
D5016-98	Standard Test Method for Sulfur in Ash from Coal, Coke, and Residues from Coal Combustion Using High-Temperature Tube Furnace Combustion Method with Infrared Absorption
D5987-96	Standard Test Method for Total Fluorine in Coal and Coke by Pyrohydrolytic Extraction and Ion Selective Electrode or Ion Chromatograph Methods
D6316-99	Standard Test Method for Determination of Total, Combustible and Carbonate Carbon in Solid Residues from Coal and Coke
D6349-99	Standard Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma-Atomic Emission Spectrometry
D6357-99	Test Methods for Determination of Trace Elements in Coal, Coke, Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission, Inductively Coupled Plasma Mass, and Graphite Furnace Atomic Absorption Spectrometries
D6414-99	Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption

The following table lists the American Society for Testing and Materials (ASTM) and International Standardization Organization (ISO) standards used for each of the analyses being performed in this project. Where several standards are published for the same type of analysis and one of them is preferable to the others, I have underlined the preferred standard. Approximate costs are shown for each measurement, with totals for measurements that involve a series of different individual measurements (proximate and ultimate analyses, for example).

Table 14 Summary of Standards for Analytical Procedures

<u>Analysis</u>	<u>ASTM No.</u>	<u>ISO No.</u>	<u>App. Cost</u>	<u>Notes</u>
Chemical Fractionation			1200	K
Proximate			72	
Total Moisture	<u>D 3173</u> ; D 3302	331	18	A, F
Ash	<u>D 3174</u>	1171	18	B
Volatile Matter	<u>D 3175</u>		18	C
Fixed Carbon	by diff	by diff	18	
Ultimate			170	
Carbon & Hydrogen	<u>D 3178</u>	625	68	D
Sulfur	<u>D 3177</u>	334, 351	34	E
Nitrogen	<u>D 3179</u>	332, 333	34	J
Oxygen	by diff	by diff	34	H
Calorific (Heating) Value	D 2015 D 3286	1928	30	G
Ash Chemistry (Si, Al, Fe, Ti, Ca, Mg, Na, K, S, P, other)	D 3682		150	I
Chlorine	D 2361	352, 587	25	G
Forms of Sulfur	D 2492	157	61	G

Notes:

- A: Samples are to be reduced in size to pass a No. 60 sieve ($< 250 \mu\text{m}$) and air dried prior to analysis.
- B: Sample should be heated to 500 °C in 1 hour, 750 °C in 2 hours, then held at 750 °C until weight stabilizes.
- C: The 'modified' procedure should be used, i.e., samples should first be heated to 600 ± 50 °C in 6 minutes then to 950 ± 20 °C for 6 minutes.
- D: Data should be reported on dry basis with hydrogen data corrected for hydrogen from moisture.
- E: Eschka method should be used. A Fisher sulfur analyzer is often used.
- F: Dry nitrogen, rather than air, should be used in procedure D 3173.
- G: These standards appear to be equally valid.
- H: A modified Unterzaucher pyrolysis technique would be preferable to computing oxygen by difference.
- I: Revisions using a lithium metaborate or lithium tetraborate flux and ICAP are commonly employed.
- J: A Carlo/Erba nitrogen analyzer is often used.
- K: Chemical fractionation includes four ash chemistry analyses, four total ash analyses, four moisture determinations, sample preparation, and extractions.

In able 15 through Table 24 summarize the following data: proximate analyses, ultimate analyses and chlorine, ash chemistry, heating value, forms of sulfur, ash fusion temperatures, and chemical formation data. Following these tables, we review and discuss the chemical fuel formation procedure that was developed in the course of this research and discuss, in some detail, the results, their consistency and associated errors, as well as the use of such data in interpreting mineral matter transformations during coal combustion.

Proximate Analyses

Table 15 Summary of Proximate Analysis data for a suite of US coals.

Fuel Name	Moisture	Ash	Volatile Matter	Fixed Carbon
Belle Ayr	25	5.9	49.12	44.98
Beulah Lignite	26.89	13.86	42.78	43.36
Black Thunder	21.3	6.46	54.26	39.28
Blind Canyon	3.3	10.4	43.58	46.03
Decker	17.99	5.11	44.03	50.87
Eagle Butte	23.74	6.4	45.55	48.05
Eastern Kentucky	1.17	10.154	36.82	53.03
Gascoigne Wood Coal	0	0	0	0
Hanna Basin	11	11.05	38.4	50.6
Illinois #6 (1)	11.83	10.13	40.95	48.91
Illinois #6 (2)	2.54	12.33	39.4	48.28
Kentucky #11	3.914	22.21	34.97	42.82
Kentucky #9	8.3	14.64	37.88	47.47
Massey Spruce	2.28	8.33	34.68	56.99
Mingo Logan	1.435	9.34	33.13	57.53
Pittsburgh #8 (1)	1.02	10.68	40.16	49.16
Pittsburgh #8 (2)	1.66	6.55	36.58	56.87
Pittsburgh #8 (3)	1.08	9	38.22	52.64
Pittsburgh #8 (4)	0	0	0	0
Pocahontas #3	0.62	4.51	18.49	77
San Miguel Lignite	18.5	52.178	30.62	17.42
Upper Freeport	0.74	21.66	24.09	54.25
Wyodak	20.48	6.22	45.55	48.24

Ultimate Analyses and Chlorine

Table 16 Summary of Ultimate Analysis Data for a Suite of US Coals

Fuel Name	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	Chlorine
Belle Ayr	74.78	5.37	0.96	0.46	18.38	0.06
Beulah	70.49	4.75	1.22	2.14	21.36	0.05
Black	74.73	5.40	1.00	0.51	18.27	0.08
Blind	81.45	6.18	1.47	0.51	10.33	0.04
Decker	76.14	5.30	1.05	0.56	16.91	0.03
Eagle Butte	71.38	5.27	1.28	0.50	21.54	0.03
Eastern	83.27	5.53	1.62	1.08	8.40	0.10
Gascoigne	0.00	0.00	0.00	0.00	0.00	0.00
Hanna	73.07	5.62	1.57	0.79	18.94	0.00
Illinois #6	76.51	5.66	1.64	4.82	11.25	0.12
Illinois #6	78.91	5.50	1.38	4.00	10.09	0.11
Kentucky	76.04	5.71	1.49	6.14	10.58	0.04
Kentucky	77.32	5.49	1.99	4.55	10.57	0.08
Massey	84.97	5.50	1.56	1.15	6.83	0.00
Mingo	86.19	5.45	1.42	0.95	5.82	0.00
Pittsburgh	80.06	5.63	1.39	5.35	7.57	0.00
Pittsburgh	84.13	5.50	1.61	1.68	6.98	0.11
Pittsburgh	84.07	5.58	1.53	3.86	4.96	0.00
Pittsburgh	0.00	0.00	0.00	0.00	0.00	0.00
Pocahontas	91.65	4.46	1.31	0.79	1.62	0.17
San Miguel	61.54	6.70	1.06	3.66	26.88	0.16
Upper	84.44	5.31	1.93	2.55	5.54	0.23
Wyodak	74.65	5.32	0.99	0.60	18.37	0.06

Ash Chemistry

Table 17 Summary of Ash Chemistry Data for a Suite of US coals.

Fuel Name	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	P ₂ O ₅	Cl
Beulah Lignite	21.23	13.97	0.42	12.25	16.36	4.46	0.22	6.50	24.60	0.00	0.00
Black Thunder	30.67	16.46	1.29	5.10	21.32	4.80	0.35	1.43	17.67	0.92	0.00
Blind Canyon	58.02	18.43	0.96	4.13	6.16	1.85	1.16	4.35	4.60	0.33	0.00
Decker	26.26	17.28	1.17	6.54	14.78	3.19	0.48	8.14	21.22	0.95	0.00
Eagle Butte	28.21	14.27	0.84	6.13	25.27	5.99	0.27	1.85	16.50	0.68	0.00
Eastern	58.20	30.67	2.08	4.88	1.16	0.42	1.00	0.17	1.29	0.13	0.00
Gascoigne	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hanna Basin	36.84	15.15	0.76	8.33	22.32	3.30	0.83	0.89	10.91	0.67	0.00
Illinois #6 (1)	46.85	16.90	0.88	20.67	5.18	0.80	2.03	1.30	5.05	0.17	0.16
Illinois #6 (2)	48.91	18.26	0.88	18.06	4.82	1.04	2.10	1.03	4.68	0.21	0.00
Kentucky #11	46.22	18.52	0.85	21.44	4.34	1.12	2.20	0.36	4.66	0.20	0.09
Kentucky #9	45.16	19.54	0.97	22.90	3.19	1.04	2.45	0.86	3.59	0.14	0.16
Pittsburgh #8	41.70	20.66	0.90	29.24	2.08	0.79	1.74	0.40	2.35	0.15	0.00
Pittsburgh #8	47.82	24.14	1.05	16.85	3.47	0.84	1.76	0.45	3.00	0.62	0.00
Pittsburgh #8	39.66	19.68	0.85	27.79	4.54	0.85	1.21	0.90	4.18	0.34	0.00
Pittsburgh #8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pocahontas #3	37.92	24.16	1.14	17.14	7.67	2.40	1.84	0.83	6.79	0.10	0.00
Roland	30.75	14.97	1.13	7.30	20.94	5.13	0.38	1.97	16.34	1.10	0.00
San Miguel	66.79	19.69	0.88	1.69	3.04	0.49	1.91	2.63	2.86	0.01	0.02
Upper Freeport	51.53	24.35	0.92	13.46	2.48	1.30	3.07	0.30	2.43	0.14	0.00
Wyodak	26.54	14.22	1.31	5.45	24.84	4.36	0.20	0.87	21.20	1.01	0.00

Heating Value

Table 18 Summary of Heating Values for a Suite of US Coals

Fuel Name	Heating Value
Belle Ayr	12781
Beulah Lignite	10040
Black Thunder	12815
Blind Canyon	13146
Decker	12483
Eagle Butte	11534
Eastern Kentucky	13254
Gascoigne Wood Coal	12000
Hanna Basin	11920
Illinois #6 (1)	12226
Illinois #6 (2)	12233
Kentucky #11	10524
Kentucky #9	11847
Massey Sprouce	13768
Mingo Logan	13805
Pittsburgh #8 (1)	13850
Pittsburgh #8 (2)	13994
Pittsburgh #8 (3)	13859
Pittsburgh #8 (4)	14000
Pocahontas #3	15052
San Miguel Lignite	5085
Upper Freeport	11830
Wyodak	11970

Forms of Sulfur

Table 19 Summary of Forms of Sulfur Analyses for a Suite of US Coals.

Fuel Name	Sulfatic	Pyritic	Organic
Beulah Lignite	0.16	0.47	1.18
Black Thunder	0.00	0.08	0.40
Blind Canyon	0.00	0.08	0.37
Decker	0.04	0.16	0.33
Eagle Butte	0.01	0.06	0.40
Eastern Kentucky	0.00	0.31	0.66
Gascoigne Wood Coal	0.00	0.00	0.00
Hanna Basin	0.03	0.19	0.43
Illinois #6 (1)	0.36	1.20	2.78
Illinois #6 (2)	0.68	0.94	2.33
Kentucky #11	0.20	2.99	1.59
Kentucky #9	0.41	1.70	1.89
Pittsburgh #8 (1)	0.15	1.81	2.82
Pittsburgh #8 (2)	0.05	0.69	0.82
Pittsburgh #8 (3)	0.03	2.07	1.42
Pittsburgh #8 (4)	0.00	0.00	0.00
Pocahontas #3	0.00	0.21	0.54
Roland	0.00	0.07	0.27
San Miguel Lignite	0.10	0.29	1.35
Upper Freeport	0.11	1.49	0.48
Wyodak	0.04	0.12	0.40

Ash Fusion Temperatures

Table 20 Summary of Ash Fusion Temperatures Data for a Suite of US Coals

Fuel Name	Reducing				Oxidizing			
	Initial	Hemisph	Spherica	Fluid -	Initial	Hemisph	Spherica	Fluid -
Beulah	774	1636	1650	1659	1714	1753	1756	1769
Black	1161	1178	1189	1210	1179	1200	1209	1243
Blind	1192	1230	1298	1449	1216	1241	1316	1468
Decker	1124	1173	1183	1201	1278	1347	1356	1368
Eagle Butte	1217	1234	1239	1245	1196	1212	1221	1231
Eastern	1620	1638	1644	1649	1627	1647	1649	1649
Gascoigne	0	0	0	0	0	0	0	0
Hanna	1196	1229	1246	1281	1246	1269	1287	1344
Illinois #6	1060	1090	1154	1253	1241	1255	1285	1366
Illinois #6	1086	1117	1183	1292	1256	1277	1265	1342
Kentucky	1076	1109	1181	1268	1268	1290	1318	1341
Kentucky	1082	1116	1188	1282	1273	1323	1354	1385
Pittsburgh	1047	1082	1179	1222	1337	1372	1381	1389
Pittsburgh	1154	1242	1306	1360	1356	1382	1399	1429
Pittsburgh	1085	1104	1138	1229	1308	1342	1369	1394
Pittsburgh	0	0	0	0	0	0	0	0
Pocahontas	1191	1249	1278	1331	1297	1313	1337	1364
Roland	1130	1156	1166	1198	1167	1191	1205	1244
San Miguel	1287	1348	1416	1515	1281	1334	1413	1517
Upper	1192	1269	1302	1336	1339	1378	1398	1429
Wyodak	1183	1212	1224	1253	1179	1207	1222	1252

Chemical Fractionation Data

Table 21 Summary of water soluble fractions from chemical fractionation data for a suite of coals.

Fuel Name	Si	Al	Ti	Fe	Ca	Mg	K	Na	S	P	Cl
Beulah Lignite	0.000	0.050	0.000	0.180	0.030	0.000	0.260	0.340	0.440	0.290	0.250
Blind Canyon	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.250
Decker	0.000	0.000	0.000	0.000	0.000	0.000	0.090	0.160	0.000	0.040	0.250
Eagle Butte	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.270	0.000	0.000	0.250
Eastern Kentucky	0.000	0.030	0.150	0.130	0.040	0.050	0.010	0.450	0.020	0.300	0.250
Gascoigne Wood	0.031	0.034	0.000	0.049	0.203	0.061	0.000	0.472	0.055	0.372	0.250
Hanna Basin	0.000	0.000	0.000	0.060	0.050	0.000	0.000	0.010	0.000	0.000	0.250
Illinois #6 (1)	0.000	0.063	0.019	0.191	0.846	0.143	0.010	0.445	0.179	0.854	0.250
Illinois #6 (2)	0.011	0.008	0.002	0.077	0.329	0.126	0.027	0.660	0.060	0.280	0.250
Kentucky #11	0.000	0.000	0.000	0.160	0.270	0.610	0.000	0.280	0.080	0.270	0.250
Kentucky #9	0.000	0.110	0.120	0.110	0.800	0.130	0.030	0.490	0.110	0.740	0.250
Pittsburgh #8 (1)	0.000	0.030	0.110	0.110	0.260	0.120	0.040	0.360	0.050	0.000	0.250
Pittsburgh #8 (2)	0.000	0.014	0.000	0.009	0.296	0.000	0.000	0.226	0.028	0.396	0.250
Pittsburgh #8 (3)	0.000	0.030	0.110	0.110	0.260	0.120	0.040	0.360	0.050	0.000	0.250
Pittsburgh #8 (4)	0.000	0.000	0.000	0.000	0.205	0.000	0.005	0.064	0.000	0.000	0.250
Pocahontas #3	0.021	0.011	0.000	0.039	0.009	0.017	0.006	0.067	0.020	0.021	0.250
San Miguel Lignite	0.000	0.000	0.000	0.055	0.000	0.000	0.047	0.266	0.011	0.255	0.250
Upper Freeport	0.000	0.000	0.000	0.020	0.660	0.090	0.000	0.320	0.060	0.680	0.250
Wyodak	0.000	0.000	0.000	0.027	0.011	0.025	0.122	0.395	0.045	0.133	0.250

Table 22 Summary of ion exchangeable fractions from chemical fractionation data for a suite of coals.

Fuel Name	Si	Al	Ti	Fe	Ca	Mg	K	Na	S	P	Cl
Beulah Lignite	0.000	0.050	0.000	0.000	0.570	0.830	0.250	0.650	0.200	0.470	0.750
Blind Canyon	0.002	0.000	0.000	0.000	0.919	0.699	0.036	0.233	0.125	0.934	0.750
Decker	0.000	0.000	0.000	0.000	0.680	0.870	0.350	0.820	0.380	0.670	0.750
Eagle Butte	0.000	0.000	0.000	0.000	0.500	0.860	0.430	0.700	0.160	0.150	0.750
Eastern Kentucky	0.000	0.000	0.030	0.000	0.480	0.180	0.040	0.100	0.020	0.360	0.750
Gascoigne Wood	0.022	0.022	0.019	0.027	0.576	0.169	0.015	0.070	0.046	0.318	0.750
Hanna Basin	0.002	0.000	0.000	0.000	0.764	0.544	0.041	0.785	0.286	0.679	0.750
Illinois #6 (1)	0.002	0.005	0.012	0.000	0.077	0.023	0.064	0.428	0.013	0.075	0.750
Illinois #6 (2)	0.058	0.060	0.064	0.027	0.515	0.351	0.059	0.004	0.097	0.467	0.750
Kentucky #11	0.003	0.029	0.015	0.000	0.667	0.091	0.080	0.281	0.085	0.685	0.750
Kentucky #9	0.001	0.000	0.000	0.000	0.124	0.024	0.006	0.262	0.012	0.204	0.750
Pittsburgh #8 (1)	0.008	0.017	0.000	0.000	0.587	0.310	0.009	0.169	0.082	0.861	0.750
Pittsburgh #8 (2)	0.001	0.000	0.034	0.000	0.369	0.108	0.016	0.274	0.027	0.406	0.750
Pittsburgh #8 (3)	0.008	0.017	0.000	0.000	0.587	0.310	0.009	0.169	0.082	0.861	0.750
Pittsburgh #8 (4)	0.001	0.011	0.000	0.111	0.633	0.463	0.025	0.213	0.142	0.817	0.750
Pocahontas #3	0.011	0.018	0.034	0.000	0.845	0.527	0.031	0.066	0.191	0.806	0.750
San Miguel Lignite	0.001	0.000	0.000	0.000	0.774	0.253	0.640	0.689	0.092	0.587	0.750
Upper Freeport	0.000	0.000	0.000	0.000	0.210	0.020	0.010	0.000	0.010	0.110	0.750
Wyodak	0.004	0.074	0.030	0.000	0.730	0.901	0.353	0.542	0.334	0.388	0.750

Table 23 Summary of acid soluble fractions from chemical fractionation data for a suite of coals.

Fuel Name	Si	Al	Ti	Fe	Ca	Mg	K	Na	S	P	Cl
Beulah Lignite	0.010	0.240	0.180	0.100	0.400	0.160	0.090	0.000	0.140	0.240	0.000
Blind Canyon	0.059	0.209	0.000	0.647	0.030	0.062	0.096	0.353	0.128	0.023	0.000
Decker	0.020	0.450	0.040	0.292	0.290	0.070	0.060	0.000	0.090	0.260	0.000
Eagle Butte	0.010	0.630	0.080	0.810	0.490	0.130	0.140	0.010	0.520	0.830	0.000
Eastern Kentucky	0.024	0.047	0.008	0.043	0.158	0.243	0.028	0.101	0.049	0.015	0.000
Gascoigne Wood	0.026	0.040	0.123	0.316	0.097	0.131	0.047	0.030	0.052	0.207	0.000
Hanna Basin	0.028	0.079	0.000	0.518	0.149	0.235	0.078	0.013	0.176	0.261	0.000
Illinois #6 (1)	0.031	0.047	0.019	0.048	0.011	0.111	0.053	0.021	0.139	0.017	0.000
Illinois #6 (2)	0.017	0.035	0.061	0.153	0.027	0.060	0.039	0.031	0.041	0.118	0.000
Kentucky #11	0.023	0.086	0.000	0.062	0.017	0.031	0.051	0.073	0.123	0.008	0.000
Kentucky #9	0.064	0.101	0.024	0.276	0.026	0.225	0.145	0.055	0.168	0.000	0.000
Pittsburgh #8 (1)	0.063	0.084	0.082	0.171	0.072	0.153	0.108	0.094	0.127	0.056	0.000
Pittsburgh #8 (2)	0.034	0.066	0.005	0.212	0.173	0.290	0.063	0.020	0.099	0.044	0.000
Pittsburgh #8 (3)	0.063	0.084	0.082	0.092	0.072	0.153	0.108	0.094	0.127	0.056	0.000
Pittsburgh #8 (4)	0.058	0.077	0.000	0.213	0.097	0.156	0.051	0.116	0.104	0.083	0.000
Pocahontas #3	0.038	0.103	0.000	0.592	0.042	0.246	0.007	0.000	0.144	0.054	0.000
San Miguel Lignite	0.005	0.072	0.070	0.481	0.177	0.140	0.059	0.004	0.039	0.116	0.000
Upper Freeport	0.020	0.060	0.000	0.331	0.060	0.290	0.030	0.000	0.090	0.090	0.000
Wyodak	0.014	0.459	0.000	0.496	0.242	0.052	0.027	0.000	0.306	0.456	0.000

Table 24 Summary of residual fractions from chemical fractionation data for a suite of coals.

Fuel Name	Si	Al	Ti	Fe	Ca	Mg	K	Na	S	P	Cl
Beulah Lignite	0.990	0.660	0.820	0.720	0.000	0.010	0.400	0.010	0.220	0.000	0.000
Blind Canyon	0.939	0.791	1.000	0.353	0.051	0.239	0.868	0.414	0.746	0.043	0.000
Decker	0.980	0.550	0.960	0.708	0.030	0.060	0.500	0.020	0.530	0.030	0.000
Eagle Butte	0.990	0.370	0.920	0.190	0.010	0.010	0.430	0.020	0.320	0.020	0.000
Eastern Kentucky	0.973	0.920	0.813	0.830	0.323	0.529	0.920	0.348	0.906	0.323	0.000
Gascoigne Wood	0.921	0.904	0.858	0.609	0.123	0.639	0.938	0.429	0.846	0.103	0.000
Hanna Basin	0.970	0.921	1.000	0.422	0.033	0.221	0.881	0.192	0.538	0.060	0.000
Illinois #6 (1)	0.967	0.885	0.951	0.761	0.066	0.722	0.873	0.106	0.669	0.053	0.000
Illinois #6 (2)	0.914	0.897	0.874	0.744	0.129	0.462	0.874	0.304	0.802	0.136	0.000
Kentucky #11	0.974	0.883	0.985	0.782	0.041	0.271	0.869	0.370	0.710	0.039	0.000
Kentucky #9	0.934	0.792	0.860	0.617	0.050	0.618	0.818	0.198	0.708	0.054	0.000
Pittsburgh #8 (1)	0.929	0.865	0.812	0.722	0.076	0.421	0.840	0.376	0.742	0.082	0.000
Pittsburgh #8 (2)	0.966	0.920	0.961	0.779	0.162	0.602	0.920	0.480	0.845	0.154	0.000
Pittsburgh #8 (3)	0.929	0.865	0.812	0.801	0.076	0.421	0.840	0.376	0.742	0.082	0.000
Pittsburgh #8 (4)	0.941	0.912	1.000	0.676	0.065	0.381	0.919	0.606	0.754	0.100	0.000
Pocahontas #3	0.930	0.868	0.966	0.369	0.104	0.210	0.956	0.867	0.645	0.118	0.000
San Miguel Lignite	0.993	0.928	0.930	0.464	0.050	0.607	0.254	0.041	0.857	0.042	0.000
Upper Freeport	0.980	0.940	1.000	0.649	0.070	0.600	0.960	0.680	0.840	0.120	0.000
Wyodak	0.982	0.467	0.970	0.478	0.017	0.022	0.498	0.062	0.316	0.022	0.000

Chemical Fractionation Procedure

The following instructions for the chemical fraction procedure comprise six parts: sample preparation, analysis of the unleached materials, analysis of the sample after each of three leachings, and characterization of the inorganics in the solid samples from each of the four stages of the procedure. An optional analysis of the leachates is also discussed which allows a mass balance to be made at each step of the procedure. The procedure and its associated logic diagram are summarized in Figure 82 and Figure 83.

Chemicals:

- 1 M Nitric Acid
- 1 M Hydrochloric Acid (HCl)
- 1 M Ammonium Acetate (NH_4OAc)

Sample Preparation

1. All samples must be small enough to be completely permeated by leaching agents (water, ammonium acetate, and hydrochloric acid). Normally this requires that the sample pass through at least a 200 mesh screen.
2. Homogenize sample by mixing in suitable container.

Unleached Material

There should be ≈ 100 g of sample (on a dry basis) at this point. At the end of this step there should be ≈ 75 g of material left for the remaining leachings, ≈ 20 g of sample labeled and saved for later inorganic analysis, the weight of the total sample before any leaching, and the moisture of the sample as weighed.

1. Weigh enough material into beaker to provide at least 100 g of dry sample.
2. Determine total weight of sample.
3. Remove and weigh approximately $1/4$ (at least 20 g) of sample.
4. Determine the moisture with a portion (< 5 g) of removed material immediately.
5. Label remaining removed material *Unleached* and set aside.

H₂O

There should be ≈ 75 g of sample (on a dry basis) at this point. At the end of this step there should be ≈ 50 g of sample (on a dry basis) left for the remaining leachings, ≈ 20 g of sample labeled and saved for later inorganic analysis, the weight of the total sample after water washing, and the moisture of the sample as weighed. From this information and the initial dry weight of the sample, the change in the dry weight induced by water washing can be calculated.

1. Add 3 ml of H₂O per gram of sample remaining in the beaker.
2. Stir overnight at room temperature.
3. Filter and rinse with distilled H₂O.
4. Determine total weight of sample.

5. Remove and weigh approximately 1/3 (at least 20 g) of moist sample.
6. Determine moisture with a portion (< 5 g) of removed material immediately.
7. Label remaining removed material *After H₂O* and set aside.

NH₄OAc

There should be $\approx$ 50 g of sample (on a dry basis) at this point. At the end of this step there should be $\approx$ 25 g of sample (on a dry basis) left for the remaining leachings, $\approx$ 20 g of sample labeled and saved for later inorganic analysis, the weight of the total sample after acetate leaching, and the moisture of the sample as weighed. From this information and the dry weight of the sample at the beginning of the acetate leaching step, the change in the dry weight induced by acetate leaching can be calculated.

1. Add 3 ml NH₄OAc per gram of water-leached sample remaining in beaker.
2. Stir overnight at room temperature.
3. Filter and rinse with distilled H₂O.
4. Repeat steps 1 through 3 twice.
5. Determine total weight of sample.
6. Remove and weigh approximately 1/2 (at least 20 g) of moist sample.
7. Determine moisture with a portion (< 5 g) of the removed material immediately.
8. Label remaining removed material *After NH₄OAc* and set aside.

HCl

There should be $\approx$ 25 g of sample (on a dry basis) at this point. At the end of this step there should be essentially no sample left to be leached, $\approx$ 20 g of sample labeled and saved for later inorganic analysis, the weight of the total sample after acetate leaching, and the moisture of the sample as weighed. From this information and the dry weight of the sample at the beginning of the acid leaching step, the change in the dry weight induced by acid leaching can be calculated.

1. Add 3 ml HCl per gram of water- and acetate-leached sample to beaker.
2. Stir overnight at 70° C.
3. Filter and rinse with distilled H₂O.
4. Repeat steps 1 through 3.
5. Determine total weight of sample.
6. Remove and weigh at least 20 g of moist sample. All of the sample may be used in this step.
7. Determine moisture with a portion (< 5 g) of the removed material immediately.
8. Label remaining removed material *After HCl* and set aside.

Ash Chemistry

There should now be four samples labeled *Unleached*, *After H₂O*, *After NH₄OAc*, and *After HCl*. The composition of the inorganic portion of these samples will allow an estimation of the modes of occurrence of each of the major inorganic elements. These analyses should be done by an atomic emission or absorption technique using an inductively coupled plasma, for example, in the analysis.

1. Submit all four samples (*Unleached*, *After H₂O*, *After NH₄OAc*, and *After HCl*) for ash analyses.
2. Submit all four samples ashed samples for inorganic analysis, which should include Si, Al, Fe, Ti, Ca, Mg, Na, K, S, P, and residual, all expressed on an oxide basis. The 'residual' is determined by difference between the sum of the oxides of the previous ten elements and the results of the total ash analysis.

Option of Analyzing Leachates in Addition to Solid Samples

At each step, the leachate and rinse water are saved in single container, weighed, and submitted to total dissolved solids and inorganic elemental analysis for the same ten elements (Si, Al, Fe, Ti, Ca, Mg, Na, K, S, and P) as are used in the ash chemistry analysis. This provides means by which a mass balance can be closed for each step.

Figure 82 Schematic illustration of the chemical fractionation procedure.

Figure 83 Logic diagram for the chemical fractionation procedure.

Analysis of the Chemical Fractionation Procedure

One issue that can simplify the chemical fractionation is determination of the overall mass change in the sample at each of the various stages by using a tracer technique. Some laboratories use silicon as a tracer to determine overall residual mass at each of the leaching stages. The use of a tracer assumes that no silicon is removed by any of the three leaching stages. We have evaluated the use of silicon as a tracer by examination of the measured silicon concentrations in the leachates (data presented in Figure 84 through Figure 86). These concentrations indicate the amount of silicon removed by each of the leaching steps and can be used to correct the change in total sample mass at each stage of the leaching. This correction is inversely proportional to the fraction of silicon removed in the leaching step. That is, if 10 percent of the silicon is leached from a sample in one of the steps, the residual total mass calculated on the basis of the silicon would be in error by 11% ($1/0.9 \times 100$).

Figure 84 Consistency of the silicon tracer technique in determining residual mass during the water leaching step of the chemical fractionation procedure. The results are inversely related to the percent loss of silicon. Less than 0.01 percent of the silicon was removed in this step. Contrast with Figure 85 and Figure 86.

The relative differences in the original mass losses (calculated by the silicon tracer technique) and the corrected values (calculated by correcting the silicon values based on the amount of silicon found in the leachates) are illustrated in Figure 84 through Figure 86 for the water

leaching, ammonium acetate leaching, and hydrochloric acid leaching steps of the procedure, respectively.

As can be seen, the water and ammonium acetate leaching procedures removed essentially no silicon. The corrections to the values calculated assuming silicon is a tracer during the water leaching step are uniformly less than 0.01 % and less than 0.001 % for most of coal samples. In the case of the ammonium acetate leaching, the errors are less than 1 % for all samples and less than 0.3 % for most. In both cases, these errors are smaller than other errors inherent in the chemical fractionation technique.

Using silicon as a tracer during the hydrochloric acid leaching step leads to errors varying from 1 to 7 % in overall mass loss. These errors are sufficiently large that they compromise the overall accuracy of the chemical fractionation technique.

Figure 85 Consistency of the silicon tracer technique in determining residual mass during the ammonium acetate leaching step of the chemical fractionation procedure. The results are inversely related to the percent loss of silicon. Less than 1 percent of the silicon was removed in this step. Contrast with Figure 84 and Figure 86.

The excellent agreement between the residual mass, as calculated by silicon tracer, and the corrected residual mass, as calculated by silicon in the leachates, indicated in Figure 84 and

Figure 85 can be misleading. These data do not imply that the residual mass can be determined with an accuracy of up to 0.001 %, for example, using silicon as a tracer. Rather, the data show that the assumption that no silicon is lost during the leaching steps is consistent with the measured concentrations of elements in the leachates. In practice, the accuracy of the silicon concentration in any one sample can rarely be determined to within less than ± 5 % without many replicated samples. This limit is primarily a consequence of inherent heterogeneity in the coal and the accuracy of the chemical techniques.

Figure 86 Consistency of the silicon tracer technique in determining residual mass during the hydrochloric acid leaching step of the chemical fractionation procedure. The results are inversely related to the percent loss of silicon. Less than 10 percent of the silicon was removed in this step. Contrast with Figure 84 and Figure 85.

The data from the acid leaching step indicate that an alternative technique for determining overall mass change should be developed. We plan to explore one such technique by drying the solid residue and subjecting it to analytical weighing at the conclusion of each of the leaching steps. In addition, moisture determinations will be made on the samples withdrawn for chemical analysis. The analytical weighing can typically be performed with four-place accuracy, which is far more accurate than the chemical analysis. Consol has agreed to investigate this procedure as an alternative to tracer techniques in another set of chemical fractionation tests. A comparison

between the new technique and closing mass balances by elemental analysis of both the solids and the leachates will be reported in the future.

A comparison between the amount of each element found in the leachate compared to the amount lost from the coal is a further check on the accuracy of the chemical fractionation technique as a whole. Having obtained analyses of the leachates, we can close mass balances on the coal directly rather than using a tracer technique to determine overall mass loss. In principle, one can choose any single element to close a mass balance and determine the overall residual mass. We initially choose silicon because it is relatively inert chemically and among the most abundant elements in the coal ash. Closing the balance on silicon allows the calculation of the concentrations of all other elements in the extract to be performed. The results of such a calculation are illustrated in Figure 87 through Figure 89 for the three leaching stages of the Wyodak coal.

Figure 87 Comparison between the elemental composition of the water leachate as analyzed and as calculated based on the solids analysis for the Wyodak coal. Compare with Figure 88 and Figure 89.

The results shown in Figure 87 through Figure 89 require some interpretation. The figures illustrate the fraction of the eight major elements found in the leachate after each of the three leaching steps for each of the nineteen coals studied. All results are shown on a sulfur- and phosphorous-free basis. The data labeled 'As Analyzed' are the results from the leachate analysis

directly. The data labeled 'Based on Solids' are derived from the chemical analysis of the solids at each leaching stage. Ideally, the two results would be identical. In many cases they are very close. However, in several cases, there are significant differences. These differences essentially always arise as a consequence of the detection limits of the techniques. For example, in many cases less than 3 % of a given element was removed in a given leaching step. The accuracy of the analysis is typically ± 3 to 5 %, so the amount removed is at the noise level of the measurement. Under these circumstances, variation due to the inherent uncertainty in the technique can change the calculated amount of material in the leachate by a factor of two even though the change in the amount of material removed from the coal is small. Therefore, large differences in these figures do not necessarily reflect a lack of precision in the chemical fraction technique.

Figure 88 Comparison between the elemental composition of the ammonium acetate leachate as analyzed and as calculated based on the solids analysis for the Wyodak coal. Compare with Figure 87 and Figure 89.

The conclusions from our chemical fractionation studies thus far are: (1) the data are reproducible within the error bars of the chemical analysis technique when care is taken to homogenize the sample and when all analyses are done in the same laboratory; (2) the accuracy of the technique as measured by comparing leachate and solid sample analyses is typically within ± 10 %, which we believe could be improved by relatively modest changes in procedure; (3) the accuracy of the technique in determining mineral composition as determined by alternative means of measuring the same mineral species is usually within ± 10 % in the relatively few cases

in which these comparisons can be made; and (4) the technique is a reliable and reasonably quantitative means of measuring important modes of occurrence of mineral phases, such as atomically dispersed material, that can not be measured by other techniques.

Figure 89 Comparison between the elemental composition of the hydrochloric acid leachate as analyzed and as calculated based on the solids analysis for the Wyodak coal. Compare with Figure 87 and Figure 88.

Combination of Inorganic Transformations and Chemical Fractionation Data

These analyses provide new and critical information for the interpretation of our mineral matter transformation investigations. For example, our previous investigations have shown that titanium is removed from coal particles during rapid coal devolatilization and that the amount released increases with increasing rate of devolatilization. On the basis of a series of detailed investigations, we postulated that the mechanism for this release involved the convective transport of atomically dispersed or very small-grained titanium in the coal. The chemical fractionation data provide quantitative and reasonably reliable indications of the amount of atomically dispersed inorganic material in the coal. (All of the material removed by either the water or the ammonium acetate leaching is assumed to be atomically dispersed.) We can now compare the correlation between atomically dispersed titanium and titanium release during devolatilization.

Figure 90 illustrates titanium release data and the amount of atomically dispersed titanium for a number of the coals analyzed during this project. There are no coals with missing data in the

figure. There are several that indicate both no mass loss and no atomically dispersed titanium. The only coals shown to release titanium in significant amounts are those that contain significant atomically dispersed titanium. The coals included in Figure 8 but not shown in Figure 90 had no chemical fractionation leachate results available.

Figure 90 Atomically dispersed titanium as determined from the chemical fractionation technique compared with the amount of titanium lost during devolatilization for many of the suite of coals studied in the MFC.

The correlation between titanium release and atomically dispersed titanium in the parent coal supports the hypothesis that devolatilization products carry the atomically dispersed inorganic components of the coal with them during rapid coal devolatilization. The chemical fractionation technique represents an *a priori* fuel analysis technique that can be used to anticipate this type of release. This is the most definitive data we have generated thus far linking the release of inorganic material during coal devolatilization to the atomically dispersed material in the coal. We hypothesize that other atomically dispersed inorganic species, notably sodium, potassium, calcium, and magnesium, may be released by similar mechanisms. We are currently analyzing our data for indications of this release mechanism and will report on it in the future.

Appendix 2: Inorganic Transformations

Thermochemical Equilibrium Predictions of Ash Deposit Chemistry

We recently completed some thermochemical equilibrium calculations examining the chemical stability of potassium-containing species relevant to biomass combustion. In the process, we believe to have discovered some errors in databases widely used in making such comparisons for coal and biomass combustion. The central issue under investigation is the relative stability of potassium silicates, sulfates and chlorides on heat transfer surfaces in boilers. Our previous data clearly indicate that potassium converts to potassium sulfate at all temperatures of relevance to heat transfer surfaces (400-1000 °C) if there is sufficient sulfur present to allow the conversion. On this basis, we successfully developed an indicator that correlated the amount of residual chlorine in the ash deposits with fuel properties.

Our intention was to show that experimental data are consistent with theoretical calculations of condensed-phase chemistry. We performed such calculations using a relatively modest database with an in-house computer code and received results that were consistent with the data and with our intuition. We then repeated the calculations using a much larger database in conjunction with a commercial computer code.

Representative results from the calculation with the commercial code are illustrated in Figure 91. The important potassium-containing chlorides and sulfates and most of the potassium-containing silicates included in the calculation are indicated in the legend. Several gas-phase species are also indicated (distinguished with a lower-case g and list separately in the legend). In total, about 150 species were included in the equilibrium calculation, only a few of which are included in the figure.

The overall conditions of the calculation are those typical of dedicated biomass combustion, including an overall oxidizing environment (about 5 moles of O₂ in product gases when expressed in the same units as are used in Figure 91). The ratios of silicon, chlorine, and sulfur atoms to potassium atoms are about 7, 0.2, and 0.35, respectively. That is, there is more than sufficient silicon to convert all of the potassium to silicates. There is sufficient chlorine to convert about one fifth of the potassium to chlorides. There is sufficient sulfur to convert about 70% of the potassium to sulfate. The predicted forms of potassium indicate which species are most stable when compared to these numbers.

Figure 91 suggests that potassium sulfate (KCl) is the most stable form of potassium at temperatures between 100 and about 500 °C. Above 500 °C, a potassium silicate is found to be the most stable. This potassium silicate, designated KAlSi₃O₈(K) in the diagram, is the mineral K-feldspar. Other compounds that are isomeric with K-feldspar and whose concentrations are included in this diagram include microcline (KAlSi₃O₈(K)), adular (KAlSi₃O₈(A)), potassium silicate glass (KAlSi₃O₈(G)), orthoclase (dimorphous with microcline) (KAlSi₃O₈(M)), sanidine (KAlSi₃O₈(S)), and maximum microcline (KAlSi₃O₈(X)). There were additional isomers included in the calculation that are not shown here. The differences between these minerals are

Figure 91 Moles of a variety of potassium-containing compounds as a function of temperature as predicted by a commercial thermochemical equilibrium code.

often very subtle and they can sometimes not be distinguished, so it is questionable which isomer is intended in many circumstances.

The anticipated behavior of these compounds was that the sulfates would be the most stable form of potassium up to temperatures at which pure potassium sulfate decomposes (about 1000 °C). Indeed, the sulfates are shown to be the most stable form at low temperatures, but the upper limit to this stability is predicted to be about 500 °C, not 1000 °C. This is a critical difference in that superheater tubes are generally 450-625 °C, and the deposits that form on them are generally 450-1000 °C. The fact that the silicates are predicted to be more stable than sulfates in this regime changes both the interpretation and the application of most of our corrosion data. Specifically, these predictions would suggest that sulfur content of fuels has little influence on potential chlorine content on superheater tubes whereas silica content may have a large impact. In addition to being inconsistent with our intuition, these observations are inconsistent with nearly all of the data collected thus far.

The stability of the silicate at temperatures below the decomposition of sulfates (about 1000°C) was surprising. It was also surprising that only one of the isomers showed this stability. Furthermore, the chemistry of this isomer so dominated the overall system that all other potassium-containing species concentrations were driven to insignificant levels. Only gas-phase HCl remains as a species of any significance except for microcline isomer at temperatures above

about 700 °C. It is well established, however, that alkali chloride gases are more stable than HCl at flame temperatures. This behavior that is inconsistent with intuition and so heavily dominated by one isomer of a common silicate drew concerned skepticism regarding the accuracy of the thermochemical data for that isomer. If these predictions are correct, they would change the interpretation of nearly all of our alkali- and chloride-related work (which is a significant fraction of the biomass work).

Upon further investigation, we found peculiar behavior in the predicted heat capacities of this isomer and another isomer with data attributed to the same reference. This is illustrated in Figure 92, where the predicted heat capacities for several of the isomers are compared.

Figure 92 Predicted heat capacities of K-feldspar and several of its isomers as derived from a commercial database. The two species designated K and X behave in a manner inconsistent with physical chemistry.

Two of the isomers show behavior that is not consistent with fundamental physical chemistry. That is, heat capacities generally can not decrease with temperature in the way indicated here when different phases of a material are treated as separate species. Two of the predicted heat capacities behave in this way, both attributed to the same reference. Upon inspection of the coefficients used to predict these heat capacities, as obtained from the commercial database, the signs of the two of the coefficients became suspect. When the sign of one of the coefficients for each species was changed, the heat capacity data were more consistent with each other and with principals of physical chemistry (see Figure 93). Clearly, the thermochemical stability of the compounds with heat capacities as indicated in Figure 93 will be very similar, as one would intuitively expect for a series of isomers that are difficult to clearly distinguish.

Figure 93 Predicted heat capacities of K-feldspar and several of its isomers after correction of the sign on one coefficient for each of the two odd-behaving species.

Based on this analysis, we discarded these data as unreliable. In fact, we suspect that the sign change was a transcription error at some point in the database and not attributed to the original source, but we have not yet verified this. However, these data appear to be in wide-spread use as we have received many comments on our conclusions consistent with the predictions of Figure 91. For now, we have simply eliminated the suspect data from the database entirely.

Elimination of the spurious data from the database changes the predicted equilibrium concentrations of the species substantially. All of the anticipated trends are observed. Specifically, potassium sulfate is the most stable form of potassium at superheater and water-wall temperatures, potassium chloride is the most stable form of chlorine at flame temperatures, and potassium sulfate decomposes to form silicates at about 1000 °C. To highlight the differences in the predictions (and to provide room for the legend), the predictions are plotted in Figure 94 on the same scale as in Figure 91. A more detailed look at the predicted concentrations is provided in Figure 95, where the legend is the same as that in Figure 94. The richly complex chemistry at high temperatures is consistent with other predictions and with expectations. The complexity of condensed-phase behavior is significant and there are good reasons to suspect that even this improved prediction is not accurate, but the relative stability of classes of compounds is almost certainly correct. The specification of activity coefficients

The conclusion from this work is that thermochemical data from reputable, commercial sources can be quite misleading if one is not careful to check the accuracy of the underlying databases.

Figure 94 Predicted equilibrium composition of potassium-containing species under the same conditions as Figure 91 but with the spurious data removed from the database. This figure is plotted on the same scale as Figure 91. See Figure 95 for a more detailed view (larger scale).

Figure 95 Predicted equilibrium composition of potassium-containing species under the same conditions as Figure 91 but with the spurious data removed from the database. See Figure 94 for legend.

Appendix 3: Deposit Properties

This appendix includes copies of papers in review that describe deposit thermal conductivity. The title, citation, and content of each paper are presented separately below.

Experimental Measurements of the Thermal Conductivity of Ash Deposits: Part 1. Measurement Technique

This paper [Robinson, Buckley et al. 2000] summarizes the experimental technique used for the first ever *in situ* thermal conductivity measurements.

Abstract

This paper describes a technique developed to make *in situ*, time-resolved measurements of the effective thermal conductivity of ash deposits formed under conditions that closely replicate those found in the convective pass of a commercial boiler. Since ash deposit thermal conductivity is thought to be strongly dependent on deposit microstructure, the technique is designed to minimize the disturbance of the natural deposit microstructure. Traditional techniques for measuring deposit thermal conductivity generally do not preserve the sample microstructure. Experiments are described that demonstrate the technique, quantify experimental uncertainty, and determine the thermal conductivity of highly porous, unsintered deposits. The average measured thermal conductivity of loose, unsintered deposits is 0.14 ± 0.03 W/(m K), approximately midway between rational theoretical limits for deposit thermal conductivity.

Introduction

Ash deposition frequently plays a dominant role in the design and operation of power generation systems that operate on coal, biomass, black liquor and other ash-forming fuels [Couch 1994]. Ash deposits form from fly ash, inorganic vapors, and some gas species that deposit or react through a variety of mechanisms [Baxter 1993; Baxter and DeSollar 1993; Baxter, Miles et al. 1993]. One effect of ash deposits is to reduce heat transfer rates to furnace walls, superheater tubes, and other heat transfer surfaces [Wall, Bhattacharya et al. 1994; Wall, Bhattacharya et al. 1995]. The magnitude of this reduction largely depends on the thickness, thermal conductivity, and emissivity of the deposits. This paper discusses the effective thermal conductivity of ash deposits; several reviews have been written on this subject [Wall, Bhattacharya et al. 1994; Gupta, Wall et al. 1997].

Heat transfer through an ash deposit occurs by conduction through both the solid and gas phases and radiation through the transparent phases. Therefore, the effective thermal conductivity, a lumped parameter, which accounts for heat transfer by all these modes, is used to characterize the heat transfer rate through a deposit. The phrase "thermal conductivity" refers to the effective thermal conductivity of the deposit.

Several investigations report measurements of the thermal conductivity of ash deposits or ash-deposit-like material [Golovin 1964; Mulcahy, Boow et al. 1966; Mulcahy, Boow et al. 1966; Boow and Goard 1969; Abryutin and Karasina 1970; Anderson, Viskanta et al. 1987; Mills and Rhine 1989; Wall, Bhattacharya et al. 1994; Robinson, Buckley et al. 1997; Robinson, Buckley

et al. 1998]. The reported values span several orders of magnitude from 0.012 W/(m K) [Golovin 1964] to 15 W/(m K) [Wall, Bhattacharya et al. 1994]. Two investigations [Golovin 1964; Boow and Goard 1969] report thermal conductivity values less than that of air, suggesting noncontinuum heat conduction in which the mean free path of a gas molecule exceeds the characteristic pore dimension of the deposit. At the other extreme, several investigators report effective thermal conductivities that exceed those of the non-porous solid material from which deposits are typically composed [Wall, Bhattacharya et al. 1994].

The thermal conductivity of ash deposits is believed to depend primarily on the deposit physical structure or microstructure [Wall, Bhattacharya et al. 1994; Baxter 1998]. For example, the denser, more-interconnected the deposit structure, the higher its thermal conductivity. Highly porous deposits of loose, unsintered, particulate matter generally have low values of thermal conductivity, potentially approaching that of air, ~ 0.06 W/(m K) at typical deposit temperatures. Solid, sintered deposits have high values of thermal conductivity, approaching that of the solid phase of the deposit (3 W/(m K) for deposits consisting primarily of silica-based material).

Composition, particle size, and temperature have also been shown to influence deposit thermal conductivity; however, the published results are not consistent on these issues [Wall, Bhattacharya et al. 1994]. These inconsistencies are not surprising considering that these parameters can both directly and indirectly influence deposit thermal conductivity. For example, the chemical composition determines the underlying thermophysical properties of the deposit materials. However, a potentially more important influence of chemical composition may be indirect through its effect on sintering propensity. Changes in deposit microstructure due to sintering are likely to be more important than variation in the thermophysical properties of the underlying deposit materials.

The importance of deposit microstructure in determining the effect of ash deposits on heat transfer rates raises concerns regarding previously reported measurements of ash deposit thermal conductivity. The majority of the reported thermal conductivity measurements are based on *post mortem* analysis techniques that destroy or significantly alter the physical structure of a deposit. Typically, powdered or pelletized ash samples are examined, which are generated using a laboratory ashing furnace, captured fly ash from a power plant, or a pulverized deposit from a boiler. These samples have chemical compositions similar to actual boiler deposits, but not the same microstructure. A few investigations have examined hybrid samples of intact, sintered deposits, and fly ash used to fill in gaps between the irregular-shaped deposit and the surfaces of the measurement device [Golovin 1964; Anderson, Viskanta et al. 1987]. Based on their analysis of these hybrid samples, Anderson et al. [Anderson, Viskanta et al. 1987] concluded that "crushing samples of porous coal ash deposits can significantly bias effective thermal conductivities." To address this issue, we have developed a novel technique that allows direct examination of the thermal conductivity of actual deposits, avoiding the problems of the previous *post mortem* analyses.

In this two-part study, we report an experimental investigation into the thermal conductivity of ash deposits. In this paper, we describe a novel experimental technique to measure the thermal conductivity of ash deposits *in situ* as they form in a pilot-scale combustor. We present

measurements of thermal conductivity of deposits formed while firing Illinois #6 coal and wheat straw and quantify the experimental uncertainty. In the second part of this study [Robinson, Buckley et al. 2000], we use this technique to examine the impacts of sintering and changes in deposit microstructure on deposit thermal conductivity. Preliminary measurements and a partial description of the experimental technique have been previously reported [Robinson, Buckley et al. 1998].

Experimental Methods

Most previous investigations of ash deposit thermal conductivity examine highly disturbed, deposit-like materials (fly ash, fuel ash, or crushed boiler deposits) in a well-characterized environment. The approach described below is guided by the hypothesis that ash deposit thermal conductivity is largely determined by deposit microstructure. Consequently, thermal conductivity measurements must be made in such a way as to minimize the disturbance of the natural deposit microstructure. To achieve this objective, we have designed a novel experiment to measure deposit thermal conductivity *in situ*, as the deposit forms, in a pilot-scale combustor.

Experimental facility

Experiments to measure the thermal conductivity of fly ash deposits were conducted using the Multifuel Combustor (MFC) at Sandia National Laboratories. A schematic diagram of the MFC is shown in Figure 96. The MFC is a pilot-scale (~ 30 kW), 4.2-m-high, down-fired, turbulent flow combustor that simulates gas temperature, gas composition, and residence times experienced by particles in entrained flow combustion systems such as pulverized-coal-fired boilers. The reactor has a 15-cm-diameter SiC reactor tube, and consists of seven 0.6-m-tall modular sections. Electrical heaters allow wall temperatures of the top six sections to follow a prescribed pattern determined by independent controllers. A more detailed discussion of the MFC is available in the literature [Baxter 1992].

The reactor tube leads to the open test section of the MFC where deposits are collected and analyzed using a variety of instruments (see Figure 96). Figure 97 shows an illustration of the configuration of the test section for the thermal conductivity experiments. The major features of this equipment are discussed in the following sections.

Experimental Procedure

A 65/35% (by mass) blend of Illinois #6 coal and wheat straw was fired in the MFC to generate an ash deposit. Utility-grind, pulverized coal (70% through a 200 mesh) was prepared separately from the wheat straw. Samples of wheat straw were ground to pass through a 0.5-mm mesh. The straw-coal blend formed part of a series of experiments examining the effects of biomass-coal cofiring on fireside combustion processes [Robinson, Junker et al. 1998]. Results from standard fuel analyses are listed in the second part of this study [Robinson, Buckley et al. 2000].

Solid fuel enters the MFC pneumatically at the top of the reactor just below the natural gas burner (see Figure 96). Under the conditions of these experiments, the residence time of a fuel particle in the combustor was approximately 1 sec, which is comparable to the residence time in commercial boilers. The fuel feed rate was set to maintain an oxygen concentration of 4% by volume (dry basis) in the combustion products at the exit of the reactor, which corresponds to the

standard utility practice of firing with 20% excess air. The natural gas burner was not operated for the experiments described in this paper.

Ash deposits are collected on an instrumented, air-cooled, stainless steel probe placed in the test section of the MFC (see Figure 96 and Figure 84). Although an ash deposit is formed over an approximately 15-cm section of the deposition probe, for thermal conductivity analysis we only examine the center 3.5 cm of the deposit, which we refer to as the deposit test section. Deposits are collected at relatively low probe temperatures (300 - 400°C) to create a loose, unsintered, particulate deposit. The average temperature of the combustion products flowing past the probe was ~ 950°C. A constant cooling air-flow rate through the probe was maintained to simulate steam flows in convection-pass tubes in utility boilers.

The gas and particle velocities through the test section of the MFC are roughly a factor of 4 smaller than typical convective pass velocities (~ 5 m/s in the MFC versus ~ 20 m/s in a power plant). Therefore, we cannot match both the Reynolds and Stokes numbers found in typical boilers. For these experiments, we choose to match the Stokes number found in typical boilers by selecting a probe with an appropriate outside diameter (2.2 cm). Deposit formation in coal-fired power plants is dominated by inertial impaction, which is a function of Stokes number. Matching Stokes numbers ensures that the size distribution of fly ash particles striking the deposition probe in the MFC is the same as the size distribution of particles hitting a superheater tube. The resulting ash deposits should have a physical structure and chemical composition similar to deposits formed in commercial coal-fired power plants. The Reynolds number of the deposition probe used in this study is roughly a factor of 10 smaller than that of a typical superheater tube, which results in lower convective heat transfer to the deposition probe in the MFC compared to a typical superheater tube. In all cases, we match the surface temperature of the deposition probe to that found in a utility boiler by adjusting the cooling air flow rate through the probe.

We rotate the deposition probe at a speed of 0.25 rpm to create a uniform, one-dimensional ash deposit. The slow rotation of the deposition probe does not measurably affect the fluid and particle flow around the probe because the rotational velocity is four orders of magnitude smaller than the velocity of the particles striking the probe surface. Therefore, we assume that the rotating the probe does not affect particle deposition and the resulting deposit microstructure. However, probe rotation does affect overall deposit shape (by design) and causes a significant periodic oscillation in the local deposit and probe temperature, as discussed later.

We use the deposit solid fraction to characterize the deposit density. For this analysis we measure the deposit mass at the end of an experiment. Combining this mass with the measured deposit volume (determined from the deposit thickness scans), we estimate the deposit bulk density. Assuming a density of 2.2 g cm^{-3} for the solid material within the deposit, we convert the bulk density to solid fraction.

Instrumentation

The experiment is designed to measure as many parameters as is possible directly, relying on analysis to combine these measurements to determine the thermal conductivity. Direct

measurements include probe surface temperature, deposit thickness, deposit surface temperature, cooling air flow rate, and cooling air temperature change. These measurements are made *in situ* while the deposit forms on the deposition probe.

Probe surface temperature is measured using four type-K thermocouples embedded in the outside of the probe wall. These thermocouples are embedded 90° apart and distributed axially along the probe test section to monitor both the azimuthal and axial variation in the probe surface temperature. We assume that temperatures at the deposit-probe interface are equal to the measured probe surface temperature.

The thickness of the deposit is measured using a range-finding laser (Selcom, Model 2207-32/180-B) mounted on a precision, position-encoded bearing. The laser scans horizontally along the probe axis. Comparing results of successive scans along the same line of sight or face of the probe, we determine the thickness and growth rate of the deposit.

Three optical pyrometers (Accufiber, Model 100C) monitor the surface temperature of the deposit. In the baseline configuration, the pyrometers are focused at the center of the deposit test section, 70°, 110°, and 170° below the flow stagnation point. The pyrometer focal area is approximately 1 mm². Periodically we change the orientation of the pyrometer to monitor surface temperatures at different locations. The pyrometers detect emitted, scattered, and reflected radiation along their line of sight. Radiation scattered and emitted by particles and radiation reflected by the deposit surface interferes with the surface temperature measurements. Shields which extend from the pyrometer lens to within ~ 4 mm of the surface of the deposit prevent particulate matter and nearly all of the scattered and reflected radiation from passing through the pyrometer line of sight. Radiation emitted by the MFC walls and from the flame ball in the combustor that is reflected by the top-half of the deposition probe (top 180°) can also significantly impact the measurements made using pyrometers. We correct for this reflected radiation by periodically rapidly shading the probe surface, and analyze the high-frequency response of the pyrometer signal to separate the reflected and emitted components of the radiation before the deposit surface cools significantly.

We use a laser pyrometer to determine the spectral emissivity of the bare probe at the beginning of each experiment and of the deposit surface at the end of each experiment. The deposit emissivity measurement is made *post mortem* immediately after removing the deposition probe from the combustor test section, before the temperature of the deposition probe has decreased by more than 100°C.

The radial heat flow through the deposit is determined using measurements of the cooling air flow rate and the cooling air temperature change across the deposit test section. The cooling air temperature change is measured using two type-K thermocouples mounted along the centerline inside the deposition probe. The thermocouples are mounted 3.5 cm apart at the outside edges of the probe test section. To prevent radial gas temperature gradients from biasing the measurements, the inside surface of the probe is rifled and screens are mounted immediately upstream of each thermocouple.

Data Interpretation

The analysis to determine deposit thermal conductivity assumes that the deposit is a cylindrical shell of uniform thickness that is defined by the outside diameter of the deposit probe and the average measured deposit thickness. Assuming steady-state, two-dimensional heat transfer through the deposit and uniform deposit thermal conductivity, the deposit temperature distribution is described by,

$$\frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r} \frac{\partial^2 T}{\partial \theta^2} = 0 \quad (1)$$

Using Equation (1), we numerically solve for the temperature distribution within the deposit using the measured azimuthal temperature distribution on the inside and outside surface of the deposit as boundary conditions. We then calculate the average temperature gradient at the inside edge of the deposit,

$$\overline{dT} = \frac{1}{2\pi} \int_0^{2\pi} \left. \frac{\partial T}{\partial r} \right|_{in}(\theta) d\theta \quad (2)$$

Combining the result from Equation (2) and the measured heat transfer rate through the deposit Q , we obtain the effective thermal conductivity of the deposit,

$$k_{eff} = \frac{Q}{2\pi r_{in} L \overline{dT}} \quad (3)$$

where $2\pi r_{in} L$ is the area of the inside surface of the deposit (r_{in} is the radius of the inside surface of the deposit, 1.1 cm, and L is the length of the probe test section, 3.5 cm).

Results and Discussion

In this section, we examine data from an experiment conducted while firing a blend of Illinois #6 and wheat straw. The purpose is to thoroughly present and discuss the experimental technique and to quantify the experimental uncertainty. We first describe time-resolved measurements of the various parameters required to evaluate the thermal conductivity of an ash deposit – deposit thickness, deposit and probe surface temperature, and heat flux. These measurements are then combined to determine the thermal conductivity of the deposit. Finally, we discuss the magnitude and sources of uncertainty of the measurements.

Surface temperature, deposit thickness, and heat flux measurements

Time-resolved measurements of deposit thickness, average deposit surface temperature, average probe surface temperature, and heat flux through the deposit are shown in Figure 98. The results indicate that a 5-mm-thick deposit formed over the course of this 2-hr experiment (Figure 98a) which created a 200°C average temperature difference between the deposit and probe surface (Figure 98b), and reduced the heat transfer through the deposit by 22% (Figure 98c). The results shown in Figure 98 are based on analyses of the data collected by the range-finding laser, optical pyrometers, and probe thermocouples. We briefly describe these data and analyses before discussing the deposit thermal conductivity measurements.

Deposit thickness

Figure 98a presents results from the deposit thickness measurements. The symbols indicate the average deposit thickness for a given scan. The range-finding laser makes a set of 4 such scans each separated by 90°, every 25 minutes. The small variation ($< 5\%$ of the average) within a set of 4 thickness scans indicates the formation of a uniformly thick deposit around the probe. The average of each set of scans, indicated by the solid line, defines the thickness of the cylindrical shell used for the analysis of deposit thermal conductivity.

The thickness results shown in Figure 98a are determined through analysis of the range-finding laser scans such as those shown in Figure 99. These scans were all taken with the same probe orientation to illustrate deposit growth along one line of sight. The range-finding laser does not directly measure deposit thickness, but rather measures the distance between the laser and the deposit surface as a function of an axial position along the probe. We must subtract a baseline, which represents the location of the probe surface, from each laser scan to determine the deposit thickness. We have already subtracted this baseline from the results shown in Figure 99. To determine this baseline, we remove some of the deposit from the outside edges of the deposition zone. To clearly define the location of the probe surface, we fit a straight line to the measured probe surface location on each side of the deposit. This procedure does not disturb the thermal conductivity measurements because the deposit test section is only the center 3.5 cm of the approximately 15-cm wide deposition zone. This technique eliminates the errors caused by thermal deformation of the probe during the experiment.

The large variations in deposit thickness are caused by actual deposit surface roughness, not measurement uncertainty. These variations, up to 2 mm, are significantly larger than the measurement uncertainty of $\pm 40 \mu\text{m}$. The measurement uncertainty is indicated by the variation in the line labeled 0 min in Figure 99.

Deposit and probe surface temperature

Figure 98a plots the average deposit and probe surface temperatures. The probe surface temperature is the average of the measurements of the 4 embedded thermocouples. The average deposit surface temperature is determined from the measurements of the 3 optical pyrometers, as discussed below. As expected, the average temperature measured by the pyrometer agrees (within experimental uncertainty) with the average probe surface temperature measured with the thermocouples at the beginning of the experiment (before deposit formation). This agreement is an important validation of the consistency of the different measurement techniques used to determine deposit thermal conductivity. As the deposit grows, the deposit surface temperature increases, while the probe surface temperature decreases. The constant cooling airflow rate in combination with the insulating effect of the deposit causes the large decline in the probe surface temperature.

Determination of the deposit surface temperature from the pyrometer data requires accounting for changes in deposit emissivity and correcting for radiation reflected by the deposit surface. To illustrate the magnitude of these corrections, the open circles in Figure 98b are the average deposit surface temperature calculated from the uncorrected pyrometer data (ignoring reflected radiation and assuming a deposit emissivity of 1). Comparing the uncorrected temperatures to

our best estimate of the actual deposit surface temperature indicates that the corrections for emissivity and reflected radiation are significant ($> 50^{\circ}\text{C}$) at the beginning of the experiment, but become negligible as the surface temperature of the deposit increases when the deposit grows. Therefore, these corrections have little impact on the measurements of deposit thermal conductivity.

Changes in the deposit emissivity have little effect on the thermal conductivity measurements. The laser pyrometer indicates that the surface emissivity varies between 0.9, the measured emissivity of the oxidized surface of the deposition probe, and 0.75, the measured deposit surface emissivity at the end of the experiment—a value consistent with previously reported measurements of deposit emissivity [Wall, Bhattacharya et al. 1994]. Over this range of values, the temperature calculated from the pyrometer data is relatively insensitive to deposit emissivity. For example, changing the deposit emissivity from 0.8 to 0.7 increases the deposit surface temperatures shown in Figure 85b by a maximum of 6°C ; a small change compared to the 200°C temperature difference that commonly exists across a deposit.

Accounting for radiation reflected by the top-half (top 180°) of the deposit causes the majority of the correction in deposit surface temperature shown in Figure 85b. This correction is significant at the early stages of the experiment when the deposit surface temperature is relatively low. As the deposit grows which causes its surface temperature to increase, the magnitude of this correction approaches zero, becoming negligible above 550°C , because the magnitude of the reflected radiation being relatively constant but the intensity of the radiation emitted by the deposit rapidly increases with temperature.

A ten-minute period of surface temperature data are shown in Figure 100 to illustrate how we determine the azimuthal temperature distribution of the deposit and probe surface. These temperature distributions are used as the boundary condition for the evaluation of equation (1). The embedded thermocouples measure the probe surface temperature at a fixed location on the rotating probe surface. Because the probe rotates, each thermocouple records a sinusoidal temperature oscillation with a period of 4 min. The 1-min phase lag between thermocouple signals is due to the azimuthal distribution of the thermocouples. The pyrometers measure the deposit surface temperature at a fixed location in laboratory coordinates. We periodically reposition the pyrometers to measure the deposit surface temperature at different angular orientations. During the 10-min period shown in Figure 100 each pyrometer was repositioned twice. For example, one pyrometer was initially focused on a location 70° below the probe leading edge. This pyrometer was then repositioned to 38° and 5° below the leading edge, at 106 and 111 minutes elapsed time, respectively. We have corrected the pyrometer data shown in Figure 100 for deposit emissivity and reflected radiation.

Figure 101 plots the azimuthal distributions derived from the data shown in Figure 100. The peak temperature occurs at the leading edge of the probe, 0° . We align and average the signals from each thermocouple to determine the average probe surface temperature as a function of θ . We fit, using least squares, a sinusoid to the optical pyrometer data to determine the deposit surface temperature distribution. The open circles shown in Figure 101 represent the average deposit surface temperature measured at 8 different angular orientations using the three different

optical pyrometers for the 10-min period shown in Figure 100. We use a sinusoid to estimate the deposit surface temperature profile because a sinusoid very accurately represents the azimuthal variation in the measurements and is consistent with theoretical analysis [Sunden 1980]. The large amplitude of the sinusoid describing the deposit surface temperature is caused by the low thermal conductivity of the deposit relative to the stainless steel probe.

Heat flux

Data shown in Figure 85c indicate that the deposit decreased the heat transfer to the cooling air by 22% (relative to the peak heat transfer rate). The heat flux increases during the first 30 minutes of the experiment, because of the change in the thermal load in the MFC that occurs at the beginning of an experiment when the solid fuel feeder is turned on. Measurements of the MFC exit gas temperature indicates that the MFC reaches thermal equilibrium in approximately 30 minutes after the turning on the solid fuel feeder.

Deposit Thermal Conductivity

Time-resolved measurements of the thermal conductivity from three different experiments are shown in Figure 102. The open circles labeled Expt. 2 represent the thermal conductivity measurements corresponding to the data presented in Figure 98 through Figure 101. Results from two additional experiments conducted under the same experimental conditions are also presented to illustrate the repeatability of the measurements. These conditions create highly porous, loose, unsintered deposits that can be easily blown or knocked off the deposition probe. The measured solid fraction of all of these deposits is 0.07. In the second part of this investigation [Robinson, Buckley et al. 2000], we examine the effects of sintering and deposit microstructure on deposit thermal conductivity.

Theoretical bounds for the thermal conductivity of porous materials provide useful reference points for the evaluation of the measurements; such bounds are discussed in detail in the second part of this study [Robinson, Buckley et al. 2000]. In Figure 102 we compare our measured values to the simplest, lowest-order bounds, which are defined based on the deposit solid fraction and the thermal conductivity of the gas and solid phases [Torquato 1992]. Treating the gas and solid phases as if they independently conduct heat in series and in parallel defines a lower and upper limit for the effective thermal conductivity, respectively. The thermal conductivity measurements shown in Figure 102 fall between these bounds. To evaluate the bounds, we use the measured solid fraction, a value of 0.06 W/(m K) for the thermal conductivity of the gas phase and a value of 3.0 W/(m K) for the thermal conductivity of the solid phase. These values are representative of air and silica-containing materials (the major component of the solid phase) at high temperature [Robinson, Buckley et al. 2000].

The average measured thermal conductivity, ~ 0.14 W/(m K), shown in Figure 102 is significantly greater than the lower bound, 0.065 W/(m K). Because these deposits are loose and unsintered, we expect that the measured thermal conductivity represent the lower extreme of the range of possible deposits that might form in real boilers. Consequently, it is unlikely that the structure of a real deposit would be such that its effective thermal conductivity is less than air, as has been suggested by some previous work [Golovin 1964; Boow and Goard 1969].

Experimental Uncertainty

Comparing the results from several identical experiments, such as those shown in Figure 102, provides an estimate of the repeatability or precision of the experiment. These experiments all produced highly porous deposits with approximately the same solid fraction, 0.07, while firing the same coal-straw blend under the same experimental conditions. The average value of the thermal conductivity from these measurements is 0.14 W/(m K) with a standard deviation of 0.016 W/(m K), and a coefficient of variation (relative uncertainty) of 11%.

The uncertainties of the underlying measurements used to determine deposit thermal conductivity are listed in Table 23. These values are determined from the published manufacturer performance data for each instrument; results from repeated instrument calibration; and analysis of data from the thermal conductivity experiments. The uncertainty of the thermocouple and cooling air flow rate measurements are the manufacturer supplied values verified by repeated calibrations. The uncertainty of the deposit thickness and optical pyrometer measurements are determined by analyzing actual experimental data. The $\pm 20^\circ\text{C}$ uncertainty listed for the optical pyrometers is the standard deviation of the measured temperature signal when the pyrometer is focused at one location relative to the probe leading edge. This value is significantly greater than the $\pm 1^\circ\text{C}$ uncertainty that can be achieved when operating the pyrometers under ideal conditions; but is much smaller than the approximately 200°C average temperature difference across the deposit. The larger uncertainty is largely due to roughness of the deposit surface. The $\pm 40\ \mu\text{m}$ uncertainty in the deposit thickness measurements is the standard deviation of a thickness scan made on a clean probe while feeding solid fuel into the reactor (data from such a scan are labeled 0 min in Figure 99). This value is significantly larger than the $\pm 2\ \mu\text{m}$ uncertainty that can be achieved when operating the range finding laser under ideal conditions, but significantly smaller than the overall deposit thickness. The larger uncertainty arises from beam steering in the hot post-combustion gases, particles (fly ash and occasionally burning char) passing through the beam path of the scanning laser, and thermal expansion of the probe as its temperature changes.

Table 25 Measurement uncertainties.

Instrument	Uncertainty
Probe Thermocouples	$\pm 5^\circ\text{C}$
Optical Pyrometers	$\pm 20^\circ\text{C}$
Cooling air flowrate	$\pm 0.3\ \text{lpm}$
Deposit thickness	$\pm 40\ \mu\text{m}$

Violation of one of the fundamental assumptions underlying the experimental technique represent the final, and potentially most significant, source of experimental error [Gavalas 1980]. For our analysis, we neglect axial heat transfer through the deposit. This assumption is not a significant source of uncertainty because the deposit has a small cross-sectional area and a low thermal conductivity; therefore, a large temperature gradient (greater than $50^\circ\text{C}/\text{mm}$) is required to create enough axial heat flux to bias the measurements. Measurements of the axial temperature profile of the deposit surface made by periodically repositioning the pyrometers indicate that there is no significant axial temperature gradient along the deposit surface.

The assumptions underlying our measurement of the heat transfer rate through the deposit are potentially the most significant source of experimental uncertainty. The experiment assumes that within the deposit test section the heat transfer rate through the deposit is equal to the heat transfer rate to the cooling air. This assumption requires that there is no significant axial heat transfer out of the deposit test section. As previously discussed, axial heat transfer through the deposit is negligible. However, axial heat conduction along the stainless steel deposition probe is a significant concern because the high thermal conductivity of stainless steel enables small temperature gradients to drive significant heat transfer. We estimate the potential error due to axial heat transfer along the deposition probe from the measurements of the axial probe surface temperature profile shown in Figure 103a, and the axial probe surface temperature gradient shown in Figure 103b. We calculate the axial heat transfer rate from the calculated axial temperature gradient, the cross-sectional area of the stainless steel wall of the deposition probe (1.14 cm^2), and the thermal conductivity of stainless steel (22 W/(m K) at 800 K).

Figure 103a shows that the deposition probe has an asymmetrical axial temperature profile with a peak temperature occurring at 100 mm, two-thirds of the distance across the 150-mm wide reactor. The profile is asymmetrical because of the cooling airflow through the probe. Centered on the peak temperature is a roughly 50-mm-wide window (see Figure 103) in which the error associated with the axial heat transfer is acceptably small—the axial heat transfer rate is less than 1.25 watts. A worst case estimate of the magnitude of this error can be made by assuming a maximum axial heat transfer rate of 1.25 watts out of each end of the test section and using 20 watts as a typical value of the measured heat transfer rate through the deposit (see Figure 98c). Under these worst case conditions, experimental error due to axial heat conduction along the deposition probe is 11%. Optimal placement of the 35-mm-wide deposit test section in 50-mm-wide window reduces this error to about 5%. We use the worst case 11% error in our overall uncertainty analysis.

To ensure that significant axial temperature gradients do not exist within the probe during an experiment, we continuously monitor the axial probe surface temperature profile. (The probe surface temperature thermocouples are axially distributed across the test section for this purpose.) If the temperature difference between any of these thermocouples is greater than 5°C the experiment is terminated.

Combining in quadrature the uncertainty of the individual measurements ($\pm 12\%$), the estimate of the experimental bias ($\pm 11\%$), and the precision of the measurements ($\pm 11\%$), we estimate that the maximum overall relative uncertainty of the thermal conductivity measurements to be $\pm 20\%$. An uncertainty of this magnitude is indicated by the vertical error bars shown in Figure 102. A typical relative uncertainty, estimated from typical instead of worst case values, is approximately $\pm 15\%$. Although the uncertainty associated with this experimental technique is larger than can be achieved by more traditional techniques for measuring thermal conductivity, the approach described in this paper may provide more accurate measurements of actual deposit thermal conductivity because of the importance of microstructure in determining deposit thermal conductivity.

Conclusions

This paper documents a novel experimental design that provides *in situ*, real-time characterization of deposit thermal conductivity under conditions that closely replicate commercial boiler operation. The experiment was designed to minimize the disturbance of the natural deposit microstructure while providing acceptable levels of experimental uncertainty. We have carefully examined potential sources of error and quantified the overall experimental uncertainty.

For the loose, unsintered deposits considered in this study, the average measured thermal conductivity of 6.14 ± 0.03 W/(m K) lies between rational theoretical bounds. We expect that these unsintered and highly porous deposits are representative of the least conductive deposits that might form in real boilers. We believe that these are the first *in situ* or real-time data of this type. The measurement technique does not significantly disturb the natural microstructure of the deposit. This capability is a significant improvement over previous experimental approaches because the thermal conductivity of ash deposits is thought to be largely determined by deposit structure. In the second part of this study [Robinson, Buckley et al. 2000], this technique is used to examine the impact of densification and sintering on deposit thermal conductivity.

Figure 96 Schematic of Multifuel Combustor.

Figure 97 Details of the probe in the experimental set-up in the test section of the Multifuel Combustor (set up is illustrated in Figure 7). Neither figure is drawn precisely to-scale, but each provides a reasonable representation of the probes and instrumentation used for these experiments.

Figure 98 Time-resolved measurements: a) average deposit thickness, b) average probe and deposit surface temperatures, and c) heat transfer rate through the test section. The open circles in (c) represent the uncorrected deposit surface temperature, as described in the text.

Figure 99 Deposit thickness measurements made with the range-finding laser system. As described in the text, the baseline representing the probe surface has been subtracted off these measurements. The labels indicate the elapsed experimental time when the scan was taken. For visual clarity, results from only three scans taken along the same probe orientation are shown. The axial location is determined by the position-encoded bearing and does not correspond to the distance across the reactor.

Figure 100 Ten minutes of probe and deposit surface temperature measurements. The numbers on the figure indicate the angle between the pyrometer focal volume and the leading edge of the probe. The vertical lines indicate approximately when the shifts in pyrometer orientation occurred. The pyrometer data have been corrected for deposit emissivity and reflected radiation. For visual clarity, measurements from two of the four probe surface temperature thermocouples and one of the three optical pyrometers are not shown.

Figure 101 Probe and deposit surface temperature as a function of azimuthal angle θ . The temperature at the leading edge of the probe corresponds to 0° ; a plane of symmetry exists along a vertical line drawn between 0° and 180° . The solid line indicates a least-squares fit ($r^2 = 0.98$) of a sinusoid to the average deposit surface temperature measurements made at each angular orientation, which are indicated by the open circles. The vertical bars indicate the uncertainty on deposit surface temperature measurement.

Figure 102 Time-resolved measurements of the thermal conductivity of several deposits formed while firing a 65/35% (by mass) blend of Illinois #6 coal and wheat straw. The measurements indicated by the open circles correspond to the data presented in Figure 98 through Figure 101. The vertical error bars indicate the maximum experimental uncertainty of $\pm 20\%$, and are only shown one set of experimental data for visual clarity.

Figure 103 a) Average probe surface temperature, and b) probe surface temperature gradient as a function of axial distance. The vertical dashed lines indicate the 50-mm-wide temperature window and the vertical solid lines indicate the optimum placement of the 35-mm-wide deposit test section within this window. The edges of the reactor tube correspond to 0 and 150 mm. The direction of cooling air flow is from left to right in this figure.

Experimental Measurements of the Thermal Conductivity of Ash Deposits: Part 2. Effects of Sintering and Deposit Microstructure

This paper [Robinson, Buckley et al. 2000] describes the analysis of thermal conductivity data and the trends in such data as deposits sinter and change microstructure.

Abstract

We report results from an experimental study that examines the influence of sintering and microstructure on ash deposit thermal conductivity. The measurements are made using a technique developed to make *in situ*, time-resolved measurements of the effective thermal conductivity of ash deposits formed under conditions that closely replicate those found in the convective pass of a commercial boiler. The technique is designed to minimize the disturbance of the natural deposit microstructure. The initial stages of sintering and densification are accompanied by an increase in deposit thermal conductivity. Subsequent sintering continues to densify the deposit, but has little effect on deposit thermal conductivity. SEM analyses indicates that sintering creates a layered deposit structure with a relatively unsintered innermost layer. We hypothesize that this unsintered layer largely determines the overall deposit thermal conductivity. A theoretical model that treats a deposit as a two-layered material predicts the observed trends in thermal conductivity.

Introduction

Ash deposits reduce heat transfer rates to furnace walls, superheater tubes, and other heat transfer surfaces in coal-fired power plants. The magnitude of this reduction largely depends on the thickness, thermal conductivity, and emissivity of the deposits. This paper examines the thermal conductivity of ash deposits under conditions similar to those found in the convective pass of utility-scale boilers; recent reviews document the current theoretical and experimental state of the art [Wall, Bhattacharya et al. 1994; Gupta, Wall et al. 1997].

Ash deposits are a complex, heterogeneous, multiphase, porous material. An extensive literature exists that discusses the heat transfer characteristics of porous materials (see, e.g., [Torquato 1992]). Like many porous materials at high temperature, both conduction and radiation can contribute to the overall heat transfer rate through the deposit; therefore, we use the effective thermal conductivity to characterize the overall heat transfer rate. The effective thermal conductivity is a lumped parameter that accounts for heat transfer by all these different modes; in this paper, the phrase "thermal conductivity" refers to the effective thermal conductivity of the deposit.

The transport properties of ash deposits and other porous materials are thought to depend strongly on the deposit physical structure or microstructure [Torquato 1992; Wall, Bhattacharya et al. 1994; Baxter 1998]. Ash deposits have a complex, highly three-dimensional microstructure. The initial structure is determined by several competing mechanisms that control deposition [Baxter, Hencken et al. 1990; Baxter and DeSollar 1993]. The deposit structure then changes on time scales ranging from minutes to days due to sintering and chemical reactions occurring at high temperature within the deposit.

Although numerous investigations report measurements of the thermal conductivity of ash deposits [Mulcahy, Boow et al. 1966; Boow and Goard 1969; Anderson, Viskanta et al. 1987; Mills and Rhine 1989; Wall, Bhattacharya et al. 1994], little experimental data exist to define quantitatively the relationship between deposit microstructure and thermal conductivity. As discussed in the first part of this investigation [Robinson, Buckley et al. 2000], the previous measurements were made on highly processed and disturbed ash samples whose microstructure may not be representative of actual boiler deposits. Second, little data are presented that describe the microstructure of the materials that were examined. Characterizing deposit microstructure is very difficult; we are aware of only two published papers that present quantitative measurements of ash deposit microstructure [Ramer and Martello 1996].

The lack of experimental data on deposit thermal conductivity and microstructure has hampered the development of realistic models for deposit thermal conductivity. Ash deposit property models are needed to simulate the effects of ash deposition on boiler performance. Existing boiler models rely on empirical expressions for evaluating deposit thermal conductivity [Richards, Slater et al. 1993; Bouris and Bergeles 1997; Senior 1997; Wang and Harb 1997; Lee and Lockwood 1999]. The simplest treatments assume a constant value for deposit thermal conductivity [Bouris and Bergeles 1996; Senior 1997]; more sophisticated approaches employ fits of experimental data [Richards, Slater et al. 1993]. Frequently the data used to determine the deposit thermal conductivity are based on measurements of surrogate materials such as sandstone and not the reported ash deposit data [Richards, Slater et al. 1993; Bouris and Bergeles 1997].

In this two-part study, we report an experimental investigation into the thermal conductivity of ash deposits. In the first part [Robinson, Buckley et al. 2000], we describe a novel experimental technique to measure the thermal conductivity of ash deposits *in situ* as they form in a pilot-scale combustor. The approach minimizes the disturbance of the natural deposit microstructure. In this second part, we employ this technique to examine the effects of densification and sintering on ash deposit thermal conductivity. SEM images are used to investigate the changes in deposit microstructure. The measured values of thermal conductivity are compared with predictions of a theoretical model.

Methods

Experiments were conducted using the Multifuel Combustor (MFC) at Sandia National Laboratories to examine the effects of sintering on the thermal conductivity of ash deposits. The experiment is designed simulate the conditions found in the convective pass of utility boilers and to minimize the disturbance of the natural deposit structure. The experimental technique is described in detail in the first part of this investigation [Robinson, Buckley et al. 2000]. In this section, we briefly describe the procedure used to sinter the deposits. We then discuss theoretical bounds for deposit thermal conductivity, and define an empirical structural parameter to measure changes in deposit microstructure.

Experimental Procedure

A 65/35% (by mass) blend of Illinois #6 coal and wheat straw was fired to generate deposits. Utility-grind, pulverized coal (70% through a 200 mesh) was prepared separately from the wheat straw. Samples of wheat straw were ground to pass through a 0.5-mm mesh. The straw-coal

blend formed part of a series of experiments examining the effect of cofiring on fireside combustion processes, including ash deposition [Robinson, Baxter et al. 1998]. Selected results from standard fuel analyses are shown in Table 26.

Table 26 Selected results from standard analysis of fuel and ash samples. The sintered deposit sample was sintered for 4 hours.

	Raw Fuel		Deposit Samples	
	Wheat Straw	Illinois #6 Coal	Unsintered	Sintered
Bulk Analysis (% mass, as rcvd)				
C	40.9	78.2	13.1	0.12
Cl	1.9	0.4	3.98	0.19
Ash	14.0	6.7	83.5	99.5
HHV (BTU/lb)	6420	13975	N/A	N/A
Ash Chemistry (mass % of ash)				
SiO ₂	37.9	49.6	48.14	51.03
Al ₂ O ₃	1.0	23.1	4.47	6.56
TiO ₂	0.1	1.3	0.20	0.24
Fe ₂ O ₃	0.5	10.8	4.05	4.47
CaO	4.0	2.7	4.86	5.08
MgO	1.5	1.4	2.17	2.28
Na ₂ O	14.4	1.4	10.01	9.31
K ₂ O	21.6	3.4	9.68	8.77
P ₂ O ₅	2.9	0.6	2.63	2.68
SO ₃	5.0	1.7	7.39	5.36
Cl	14.5	N/A	N/A	N/A
CO ₂	0.1	N/A	N/A	N/A

Experiments are conducted in two stages to examine the effects of sintering on deposit thermal conductivity. During the growth stage, deposits are collected at relatively low probe surface temperatures (300 to 450°C) to create a loose, unsintered, particulate deposit. After a sufficiently thick deposit forms, the solid fuel feed is turned off and the deposit is sintered by increasing the ambient gas (and deposit) temperature by firing the MFC natural gas burner, injecting natural gas into the lower furnace immediately above the deposit, and increasing the MFC wall temperature. We refer to this second stage of the experiment as the sintering stage.

We use the deposit solid fraction as a measure of the extent of deposit sintering. The solid fraction, ϕ , is the ratio of the volume of the solid phase to the total volume of the deposit. We determine the solid fraction from the deposit mass measured at the end of an experiment, the deposit volume determined from the deposit thickness scans, and an assumed density of the deposit solid phase of 2.2 g cm⁻³. We assume that the mass of the deposit does not change during

the sintering phase of an experiment; therefore, we can determine the time history of deposit solid fraction by monitoring the changes in deposit volume while sintering.

At the end of each experiment the deposit is removed from the probe for further analysis. A standard ash analysis provides the bulk elemental composition of the deposit. SEM analysis generates electron micrographs of deposit microstructure. Two procedures were used to prepare samples for SEM analysis. The first procedure involves impregnating deposit pieces in epoxy. The samples are then cross-sectioned, polished, and carbon coated; we refer to these samples as potted samples. The potted samples are cross-sectioned normal to the probe surface to allow examination of the radial variations in microstructure. Mounting the samples in epoxy allows for quantitative image analysis because the SEM only detects the solid and void space that intersects the cross-sectioned plane. The second procedure involves directly carbon coating deposit pieces; we refer to these samples as unpotted samples. The unpotted samples are positioned in the SEM to allow detailed examination of the inside and outside surface of the deposit.

Theoretical Limits and the Structural Parameter

Theoretical limits for the effective thermal conductivity of porous materials are useful reference points for evaluation of the measurements. We compare the measured values of deposit thermal conductivity to the simplest, lowest-order theoretical bounds [Torquato 1992]. Treating the gas and solid phases as if they independently conduct heat in parallel defines an upper limit for the effective thermal conductivity,

$$k_{up} = (1 - \phi)k_g + \phi k_s, \quad (1)$$

where ϕ is the deposit solid fraction, k_g is the gas phase thermal conductivity, and k_s is the solid phase thermal conductivity. Treating the gas and solid phases as if they conduct heat in series defines a lower limit,

$$k_{low} = \frac{k_s k_g}{(1 - \phi)k_s + \phi k_g}. \quad (2)$$

Although many higher-order (tighter) bounds have been derived for porous materials [Torquato 1992], these bounds typically assume an isotropic structure and, therefore, cannot be applied to ash deposits, which are commonly highly anisotropic. Others [Torquato 1992] discuss higher-order bounds for anisotropic materials; application of these bounds requires detailed information about the deposit microstructure.

Equations (1) and (2) are intended to provide a rational basis for comparison; they are not rigorous theoretical bounds for the thermal conductivity of ash deposits. For example, deposits with very small pore sizes (smaller than the mean free path of air) could have an effective thermal conductivity below the lower limit defined by equation (2); radiation can result in effective thermal conductivity greater than the upper limit defined by equation (1).

We need values for the thermal conductivity of the gas and solid phase material to evaluate the theoretical limits. We use a value of 0.06 W/(m K) for k_g , which is comparable to the thermal conductivity of air at typical deposit temperatures. Assigning a thermal conductivity value to the

solid phase is more difficult because the deposit chemical composition is largely unknown. Ash compositions (for example, see Table 26) are commonly reported on an oxide basis as a matter of practice; the analytical techniques do not provide any information on chemical composition. Previous work indicates that the thermal conductivity of the deposit solid phase cannot be approximated using a weighted average based on the mass proportion of the oxides [Wall, Bhattacharya et al. 1994], although it presumably could be approximated as the weighted average of the species actually present in the deposit. Because these species are not precisely known but generally are dominated by silica and aluminum silicates, we use a constant value of 3 W/(m K) for k_s , which is representative of the thermal conductivity of silica-containing materials at high temperature [Touloukian and Ho 1989]. Using the aforementioned values for k_g and k_s , the upper limit is on average 9 times greater than the lower limit, with a maximum difference of a factor of 13. The large difference between the lower and upper bounds is characteristic of porous materials such as ash deposits that consist of two phases with very different thermal conductivities and underscores the importance of structural information in determining deposit thermal conductivity.

Since the theoretical limits defined by equations (1) and (2) correspond to extremes in deposit microstructure, we use these limits define an empirical structural parameter,

$$\chi(\phi) = \frac{k_{\text{meas}}(\phi) - k_{\text{low}}(\phi)}{k_{\text{up}}(\phi) - k_{\text{low}}(\phi)}, \quad (3)$$

where k_{meas} is the measured value of deposit thermal conductivity. This parameter provides a useful metric for the interpretation of the experimental results that reflects the microstructure of the deposit. Assuming Equations (1) and (2) define rigorous bounds, the structural parameter varies between 0 and 1 ($0 \leq \chi(\phi) \leq 1$). Values close to 0 indicate a deposit with a more layered structure whereas those close to 1 indicate a deposit with a more columnar structure. This parameter is a global parameter that accounts for the effects of any non-uniformity on the net heat transfer rate through the deposit. Both the solid fraction and the structural parameter are required to uniquely define the deposit thermal conductivity.

Results and Discussion

A series of experiments were conducted while firing the 65/35 blend of Illinois #6 coal and wheat straw to examine the effects of sintering and densification on deposit thermal conductivity. In this section we first describe the measurements of deposit thermal conductivity. We then discuss the relationship between the trends in deposit thermal conductivity and the changes in deposit microstructure, deposit temperature, and deposit chemical composition. Finally, we compare the thermal conductivity measurements to predictions of a theoretical model.

Measurements of Deposit Thermal Conductivity

Figure 104 presents measurements that illustrate the effect of sintering on deposit thermal conductivity. Plotted are time-resolved measurements of the average deposit thickness (Figure 104a), the average probe and deposit surface temperatures (Figure 104b), the deposit solid fraction (Figure 104c), the deposit structural parameter (Figure 104d), and the deposit thermal conductivity (Figure 104e). The experiment was conducted in two stages, which are separated by

the heavy vertical line in Figure 104. The growth stage of the experiment occurred between 0 and 2.5 hours elapsed time during which a highly porous, unsintered deposit was collected. At the end of this first stage, the solid fuel feeder was turned off and the deposit temperature was increased to induce sintering and densification. The sintering stage of the experiment lasted for approximately 12 hours.

The deposit formed during the growth phase of the experiment (0 – 2.5 hours) has an average thermal conductivity of 0.14 W/(m K) and a measured solid fraction of 0.07. This very porous deposit consisted of loose, unconsolidated particles, which can easily be blown or knocked off the probe. The unconsolidated nature of the deposit is due to the low average deposit temperature of ~ 450°C during the growth phase of the experiment. We expect that the thermal conductivity of such a deposit represents the lower extreme of the range of possible deposits that might form in real boilers.

During the sintering phase of the experiment (2.5 – 14.5 hours), the deposit thermal conductivity increased by a factor of 2.3 from 0.14 to 0.31 W/(m K), and the average deposit temperature was increased to more than 650°C. The degree of sintering is indicated by the deposit solid fraction; the higher the solid fraction the more sintered the deposit. Sintering increased the deposit solid fraction by a factor of 4 from 0.07 to 0.28, creating a deposit that consisted of a well-consolidated, friable material that had to be scraped from the probe. Throughout the entire experiment the measured values of deposit thermal conductivity fall between the theoretical limits.

There are two important points to be made regarding the changes in deposit thermal conductivity observed during the sintering stage of the experiment. First, the overall trend in the measured deposit thermal conductivity more closely follows the lower theoretical limit than the upper limit. This is reflected by the falling value of the structural parameter (Figure 104d) throughout the majority of the sintering phase of the experiment, which indicates that sintering causes the measured deposit thermal conductivity to approach the lower limit. Second, the changes in deposit thermal conductivity observed during the sintering phase of the experiment occur in two distinct stages. The majority of the increase in the deposit thermal conductivity occurs between 2.5 through 4.5 hours elapsed time. During this period, the deposit solid fraction increases from 0.07 to 0.11 and the deposit thermal conductivity increases from 0.14 to 0.26 W/(m K) – 70% of the total increase in deposit thermal conductivity, but only 20% of the total increase in deposit density. Between 4.5 through 14.5 hr elapsed time the deposit density increased by more than a factor of 2, but the thermal conductivity only slightly increased.

The trends in thermal conductivity shown in Figure 104 can be attributed to one or more of the several changes that occurred during the sintering phase of the experiment. Sintering significantly altered the deposit microstructure, increasing the deposit density by a factor of 4. The average deposit temperature rose by approximately 200°C during the sintering phase of the experiment. Sintering also changed the deposit chemical composition. In the next three sections, we discuss in detail the effects of these changes in order to understand the observed trends in deposit thermal conductivity.

Sintering and deposit microstructure

Ash deposit thermal conductivity is thought to depend strongly on the deposit microstructure because the thermal conductivity values of typical deposit solid phase materials are two to three order of magnitude greater than those of deposit gas phase materials. Deposit solid fraction provides the simplest measure of the changes in deposit structure that occur during sintering. Although solid fraction does not provide any structural information, it does indicate the deposit density. The deposit solid fraction (or, equivalently, porosity or deposit density) is often used as a predictor for the effects of sintering on deposit thermal conductivity [Richards, Slater et al. 1993; Wall, Bhattacharya et al. 1994].

A plot of the measurements of deposit thermal conductivity as a function of solid fraction is shown in Figure 105. The results indicate that increases in deposit density due to sintering are not necessarily accompanied by increases in deposit thermal conductivity. Therefore, deposit solid fraction by itself is a poor predictor of the effects of sintering on deposit thermal conductivity. One must combine solid fraction with some information on the deposit microstructure to predict the changes in thermal conductivity. The trends shown in Figure 104 and Figure 105 indicate that sintering changes the deposit microstructure in such a way to offset any potential increase in thermal conductivity due to increased deposit density.

To determine the effects of sintering on deposit microstructure, SEM analysis was performed on four deposits created under identical experimental conditions and then sintered for different periods of time (0, 1, 4, and 12 hours). Figure 106 shows time-resolved measurements of deposit thermal conductivity and solid fraction from these experiments. The changes in deposit solid fraction indicate that the deposits sintered at the same rate. The thermal conductivity measurements all exhibit the same trend – a significant increase in deposit thermal conductivity occurs during the initial stages of sintering; further sintering has relatively little impact on the deposit thermal conductivity.

Electron micrographs are shown in Figure 107 and Figure 108 that illustrate the changes in deposit microstructure that occur during the sintering phase of the experiment. These micrographs were taken at low magnification (50X and 35X) in order to assess the large-scale changes in deposit structure. Figure 107 shows the cross-section of the unsintered deposit and the deposit sintered for 12 hours mounted in epoxy. Figure 108 shows the inside and outside surfaces of unpotted pieces of all four deposits. We suspect that the images over-estimate the extent of sintering on the inside surface of the deposit because the deposits are removed from the deposition probe for SEM analysis.

Qualitative comparison of the images shown in Figure 107 reveals dramatic structural differences between an unsintered and a sintered deposit. The unsintered deposit consists primarily of distinct particles that appear isolated from their neighbors. Although the solid regions may appear isolated in the two-dimensional image, it is important to realize that the solid phase forms a continuous structure in three dimensions. The structure of the unsintered deposit appears to be isotropic – without a label one cannot tell which is the inside or outside surface of the deposit. The cross-section of a sintered deposit shows a significantly different structure – instead of distinct particles, there is a substantial, interconnected solid phase. The sintered deposit clearly

has an anisotropic structure with large plate-like features present near the outside surface of the deposit. The mean feature size in the sintered deposit is significantly larger than that in the unsintered deposits.

Image analysis techniques were used to quantify the differences in the microstructure of the unsintered and sintered deposits shown in Figure 107. The results of this analysis indicate that sintering creates a deposit with a layered structure. For example, using the procedures described by Ramer and Martello [Ramer and Martello 1996] we examined the radial variations of deposit solid fraction. The solid fraction of the unsintered deposit is essentially uniform; the measured solid fraction of the inside and outside half of the unsintered deposit is 0.09 and 0.11, respectively. In comparison, the deposit sintered for 12-hours exhibits significant radial variations in solid fraction; the measured solid fraction of the inside quarter and outside three quarters of the sintered deposit is 0.15 and 0.32, respectively. We expect the formation of a layered deposit structure during the sintering stage of the experiment because the large temperature gradients (up to 100 °C/mm) result in a wide range of sintering rates across a deposit. The solid fraction values determined with the image analysis technique when applied to the entire deposit compare favorably to those determined from the measurements of deposit mass and deposit volume.

The electron micrographs of the unpotted deposit samples shown in Figure 108 provide additional evidence that a layered deposit structure forms during the sintering stage of the experiment. One cannot differentiate between the inside and outside surface of the unsintered deposit, which suggests a uniform deposit structure. Evidence of a layered structure can clearly be seen after only 1 hour of sintering. After 1 hour the inside surface of the deposit appears unchanged while numerous bridges have formed between particles found on the outside surface of the deposit. After 4 hours of sintering substantial bridges have formed between all of the particles on the outside surface, while the inside surface has a rough, porous appearance. After 4 hours of sintering there is some evidence of sintering at the inside deposit surface. After 12 hours of sintering the outside deposit surface has a smooth, interconnected structure while the inside surface still has a rough, angular structure. All of these images reveal the complex, three-dimensional structure of ash deposits.

The trends in the structural parameter shown in Figure 104d also indicate that a layered deposit structure forms during the sintering phase of the experiment. During the initial stages of sintering the structural parameter increases indicating that the measured thermal conductivity is trending towards the upper limit. This suggests that the sintering initially creates a deposit with a more columnar structure. Subsequent sintering causes the structural parameter to decrease indicating that the measured thermal conductivity is trending towards the lower limit. The physical interpretation of this trend is that sintering creates in a more layered deposit structure. The time history of the structural parameter indicates that layering occurs throughout most of the sintering phase of the experiment.

The changes in the deposit microstructure apparent in Figure 107 and Figure 108 provide a compelling explanation for the trends in deposit thermal conductivity. The hypothesis is that the structure of the solid phase largely determines the thermal conductivity of a deposit. During the

initial stages of sintering, the contact area between particles rapidly increases as point contacts between particles fuse together resulting in increased deposit thermal conductivity. This occurs primarily in the hotter outer layers of the deposit and causes the sharp increase in thermal conductivity observed during the initial stages of sintering. At later times, a relatively unsintered inner layer next to the cool probe surface dominates the overall deposit thermal conductivity. During this period, the contact area between particles no longer limits the conduction through the solid phase and the overall deposit thermal conductivity is limited by layered deposit structure that requires significant sintering to substantially alter.

Sintering and Deposit Temperature

The average deposit temperature rose by $\sim 200^\circ\text{C}$ during the sintering phase of the experiment. It is important to determine if this temperature rise is responsible for some or all of observed increase in deposit thermal conductivity independent of the changes in structure. At high temperatures, radiation can increase significantly the heat transfer rate through the deposit, which, in turn, increases the effective deposit thermal conductivity. The thermal conductivity of gas and some solid phase materials also increase with temperature.

Measurements of deposit thermal conductivity made at the end of the experiment as the deposit cooled down suggest that the increase in deposit temperature during the sintering phase of the experiment had relatively little direct effect on the deposit thermal conductivity. For example, reducing the average deposit temperature from 600°C to 450°C reduced the effective thermal conductivity of the deposit by less than 10% from 0.31 to 0.29 W/(m K). Of course, the increase in temperature during the sintering phase of the experiment plays a critical, but indirect role, on the changes in thermal conductivity because high temperatures are required to drive the sintering and chemical reactions that cause changes in deposit structure.

Sintering and deposit composition

We performed standard elemental analysis on bulk deposit samples to evaluate the changes in chemical composition that occurred during the sintering phase of the experiment. As previously discussed, changes in deposit chemical composition can effect the thermal conductivity of the solid phase material. The bulk elemental composition of an unsintered deposit and a deposit sintered for 4 hours are shown in Table 26. The data suggest that carbon and chlorine containing species decompose during the sintering phase of the experiment. The decomposition of these species is consistent with thermodynamic equilibrium calculations; for example, at high temperatures, CaO is thermodynamically favored relative to CaCO_3 . The decomposition of the deposit carbon and chlorine species is likely to have little affect on the overall thermal conductivity of the deposit solid phase. First, carbon and chlorine make up only 17% of the deposit solid phase; therefore, loss of this material will likely have little effect on the solid phase thermal conductivity and the deposit solid fraction. Second, decomposition will likely create species with very similar values of thermal conductivity to the original species.

Implications for Model Development

Models for deposit thermal conductivity are needed to simulate the effects of ash deposition on utility boiler performance. At present, the most sophisticated models for deposit thermal conductivity account for changes in deposit density; they do not account for changes in deposit

microstructure [Richards, Slater et al. 1993]. The measurements presented here indicate that models must account for changes in microstructure. The fact that sintering creates a layered microstructure suggests a simple conceptual framework for predicting the effects of sintering on deposit thermal conductivity. In its simplest formulation a deposit can be treated as a material with two layers and an overall thermal conductivity of

$$k = \frac{1}{\frac{L}{k_{un}} + \frac{(1-L)}{k_{si}}}, \quad (4)$$

where L is the thickness of the unsintered layer normalized by the total deposit thickness, k_{un} is the thermal conductivity of the unsintered, inner layer of the deposit, and k_{si} is the thermal conductivity sintered, outer layer of the deposit. Equation (4) can easily be generalized to account for a deposit with more layers; however, as will be shown, the two-layer formulation predicts the effects of sintering on deposit thermal conductivity observed in these experiments. Calculations of the overall deposit thermal conductivity using equation (4) are shown in Figure 109. Curves are presented as a function of k_{si} for three different values of L . A constant value of 0.15 W/(m K) is used for k_{un} , this value corresponds to the measured deposit thermal conductivity at the beginning of the sintering phase of the experiment. The value of k_{si} varies between k_{un} and 3 W/(m K), the thermal conductivity of the deposit solid phase material. The calculations shown in Figure 109 describe the following conceptual scenario for the effects of sintering on deposit thermal conductivity. The initial deposit has a uniform ($k_{si} = k_{un}$) thermal conductivity of 0.15 W/(m K), which corresponds to the minimum value shown in Figure 109. Sintering then occurs in the hotter outer regions of the deposit, which causes k_{si} (the thermal conductivity of the outer layer of the deposit) to increase while k_{un} (the thermal conductivity of unsintered, inner layer) remains constant. The more sintered the deposit the higher the value of k_{si} implying that time increases from left to right in Figure 109.

Figure 109 indicates that the two-layer model qualitatively predicts the trends in the measured deposit thermal conductivity shown in Figure 104e. The initial stage of sintering, corresponding to the change in k_{si} from 0.15 to 1 W/(m K), causes a substantial increase in the overall deposit thermal conductivity. Subsequent sintering, corresponding to values of k_{si} greater than 1 W/(m K), has relatively little effect on the overall deposit thermal conductivity. The fact that increases in k_{si} beyond 1 W/(m K) have little impact on the overall deposit thermal conductivity indicates that after the initial sintering stage, the only way to increase the overall deposit thermal conductivity is to increase k_{un} , the thermal conductivity of the unsintered layer. Sensitivity analysis indicates that if the unsintered layer is more than 20% of the deposit thickness, it largely determines the overall deposit thermal conductivity.

In order to compare predictions of the two-layered model to the measurements of deposit thermal conductivity we need estimates for k_{un} , k_{si} , and L from an actual deposit. Sensitivity analysis reveals that the critical parameter is k_{un} if L is greater than 0.2 and the ratio of k_{si} to k_{un} is greater than about 3. We use a constant value of 0.15 W/(m K) for k_{un} , which is the measured deposit thermal conductivity at the beginning of the sintering phase of the experiment. We assume a constant value of 0.4 for L . Finally, we assume that k_{si} varies linearly with the solid fraction of

the sintered layer. The slope and intercept of this relationship is defined by the measured solid fraction and thermal conductivity of the deposit at the start of the sintering phase of the experiment and of the solid phase material. The time history of the sintered layer solid fraction is determined from the measurements of the overall deposit solid fraction (Figure 104c), L , and assuming the solid fraction of the unsintered layer remains constant. The predictions of the overall deposit thermal conductivity are relatively insensitive to the assumed functional form of k_{si} .

Figure 110 compares predictions of the two-layered model to the measurements of deposit thermal conductivity shown in Figure 104e. The accuracy of the predictions provides additional evidence for the importance of a layered deposit structure in determining the effects of sintering on deposit thermal conductivity. The results shown in Figure 110 also underscore the dominant role that an unsintered layer with a low value of thermal conductivity can have on the overall deposit thermal conductivity. After 4 hours of sintering, the overall deposit thermal conductivity is limited by k_{un} . The effect of a low thermal conductivity unsintered layer explains why only small changes in deposit thermal conductivity were observed in our experiments after substantial sintering.

Conclusions

This paper describes experiments conducted to examine the effects of sintering and changes in microstructure on ash deposit thermal conductivity. The experiments were performed on deposits formed while firing a blend of Illinois #6 coal and wheat straw. The measurements were made *in situ* while the deposits formed and then sintered in a pilot-scale combustor. The deposits are representative of those found in the convective pass of a utility boiler. Initial stages of sintering are characterized by a substantial increase in deposit thermal conductivity; subsequent sintering has little effect on deposit thermal conductivity. Analysis of SEM images of deposit samples indicates that sintering creates a layered microstructure. Sintering significantly changes the microstructure of the outer layers, but has relatively little effect on the innermost layer of the deposit located adjacent to the cool deposition probe. Theoretical analysis that treats the deposit as a two layered material predicts the observed trends in deposit thermal conductivity. The model indicates that a low thermal conductivity layer largely determines the overall thermal conductivity of the deposit. Therefore, after the initial stages of deposit sintering, the thermal conductivity of the innermost, unsintered layer must be increased to increase the overall thermal conductivity of the deposit.

This study represents a significant advance in our ability to examine the impact of sintering on deposit thermal conductivity. By making *in situ* measurements that minimally disturb the natural deposit microstructure, we were able for the first time to examine the effects of sintering on deposit microstructure and deposit thermal conductivity. Although it is generally recognized that sintering creates layered deposits, these measurements are the first, to our knowledge, that quantifies the effects of layering on real deposits. Anderson et al. [Anderson, Viskanta et al. 1987] present data which show that sintering increases the thermal conductivity of the outer layers of a deposit. However, their data do not reveal the significant effect of the unsintered inner layer on the overall deposit thermal conductivity. This is likely due to the fact that their measurements were made using crushed deposit material, which probably do not have the same

structure as actual deposits. In addition, the temperature of the inside surface of the deposit exceeded 750°C, which is much higher than typical superheater tube temperatures in actual boilers. This high temperature likely caused substantial sintering of the innermost deposit layer.

The results demonstrate that, for the ash deposits considered here, thermal conductivity depends strongly on deposit microstructure. The deposit solid fraction (or, equivalently, porosity or deposit density) cannot be used by itself as a measure of the effects of sintering on deposit thermal conductivity. This has implications on the development of models for deposit thermal conductivity. Models must account for effects of changes in microstructure on deposit thermal conductivity; current models do not account for these effects. The most sophisticated models use deposit porosity or solid fraction as the measure of the effects of sintering [Richards, Slater et al. 1993]. For the deposits examined in this study, this is not a valid approach. The success of the simple two-layered model in predicting the observed changes in deposit thermal conductivity suggest that such a model may be a useful approach for accounting for the effects of changes in deposit microstructure on deposit thermal conductivity. Predictions of this model critically depend on the thermal conductivity of an unsintered layer; even a very thin layer with a low thermal conductivity can significantly limit the overall thermal conductivity of a deposit.

Figure 104 Measurements of (a) average deposit thickness, (b) average probe and deposit surface temperature, and (c) deposit solid fraction, (d) deposit structural parameter, and (e) deposit effective thermal conductivity as a function of time. This deposit was created while firing the blend of Illinois #6 and wheat straw. Figure (e) also compares the measured values to theoretical limits for deposit thermal conductivity. The thick vertical line indicates the transition between the growth and sintering phases of the experiment. Vertical bars in (e) indicate estimate of experimental uncertainty.

Figure 105 Thermal conductivity measurements and theoretical limits as a function of deposit solid fraction. Data are from the same experiment as those shown in Figure 104. Vertical bars show estimate of experimental uncertainty on selected data points. Time increases from left to right, but note that solid fraction does increase linearly with time as shown in Figure 104c.

Figure 106 Measurements of (a) deposit solid fraction, and (b) deposit effective thermal conductivity as a function of time. As described in the text, these measurements were conducted under the same experimental conditions, but the experiments were terminated after different periods of sintering to examine the changes in deposit microstructure. The vertical line at 0 hours elapsed time indicates the start of sintering portion of the experiment. Data for the deposit sintered for 12 hrs are also shown in Figure 104 and Figure 105. The theoretical limits are calculated from the solid fraction of the deposit sintered for 12 hrs. The elapsed time for some of the thermal conductivity measurements has been slightly shifted for visual clarity. Vertical bars indicate estimate of experimental uncertainty on selected data points.

(a) Unsintered deposit

(b) Sintered deposit

Figure 107 Electron micrographs of cross-sections of an unsintered deposit and a deposit sintered for 12 hours impregnated in epoxy. The bright regions in these images correspond to cross-sectional profiles of deposit solid phase material; the dark regions correspond to void space. The entire cross-section of the sintered deposit and part of the cross section of the unsintered deposit is shown in the figure.

INSIDE SURFACE

OUTSIDE SURFACE

0 hr

1 hr

4 hr

12 hr

600μm 35X

600μm 35X

Figure 108 Electron micrographs of the inside and outside surface of deposits that have been sintered for 0, 1, 4, and 10 hours. These deposit samples were directly carbon coated and analyzed with the SEM, as described in the text.

Figure 109 Calculations of the overall deposit thermal conductivity with the two-layered structure model as a function of the thermal conductivity of the sintered layer, k_{si} . Curves are shown for three different values of the nondimensional thickness of the unsintered layer, L , and a constant value of the unsintered layer, k_{un} .

Figure 110 Comparison of the measurements of deposit thermal conductivity shown in Figure 1e to predictions of the two-layered structure model as a function of time. The values of k_{un} , k_{si} , and L used to evaluate the model are described in the text. Elapsed time corresponds to the sintering stage of the experiment. Vertical bars indicate estimate of experimental uncertainty on selected data points.

Appendix 4. Publications

The following publications were developed from work supported in whole or in part by NETL at Sandia National Laboratories as part of this project.

1. Abbott, M. F., Douglas, R. E., Fink, C. E., Deluliis, N. J. and Baxter, L. L. (1993) "A Modeling Strategy for Correlating Coal Quality to Power Plant Performance and Power Costs," In *Engineering Foundation Conference on The Impact of Ash Deposition on Coal-Fired Plants* Solihull, England.
2. Abbott, M. F., Douglas, R. E., Fink, C. E., Deluliis, N. J. and Baxter, L. L. (1994) In *The Impact of Ash Deposition on Coal-Fired Plants* (Eds, Williamson, J. and Wigley, F.) Taylor & Francis, Washington D.C., pp. 165-176.
3. Baxter, L. L. (1993) "Ash Deposition During Biomass and Coal Combustion : a Mechanistic Approach," *Biomass & Bioenergy*, **4**, 85-102.
4. Baxter, L. L. (1993) "In Situ, Real-Time Emission FTIR Spectroscopy as a Diagnostic for Ash Deposition During Coal Combustion," In *Engineering Foundation Conference on The Impact of Ash Deposition on Coal-Fired Plants* Solihull, England.
5. Baxter, L. L. (1994) "The effect of Low-NO_x Firing on Fireside Performance," In *International Joint Power Generation Conference* Scottsdale, AZ, pp. 211-220.
6. Baxter, L. L. (1994) In *Coal-Blending and Switching of Low-Sulfur Western Coals* (Eds, Bryers, R. W. and Harding, N. S.) ASME, New York, pp. 255-264.
7. Baxter, L. L. (1994) "Nitrogen Release During Coal Combustion: Coal Rank and Extent of Combustion Trends," *Energy & Fuels*, .
8. Baxter, L. L. (1995) In *Encyclopecia of Energy Technology and the Environment*, Vol. 1 John Wiley & Sons, Inc., New York, pp. 306-321.
9. Baxter, L. L. (1995) "The effect of Low-NO_x Firing on Fireside Performance," In *The Economic and Environmental Aspects of Coal Utilization VI* Santa Barbara, CA.
10. Baxter, L. L. (1995) In *The Impact of Ash Deposition on Coal-Fired Plants* (Eds, Williamson, J. and Wigley, F.) Taylor & Francis, Washington D.C., pp. 313-323.
11. Baxter, L. L. (1996) "Influence of ash deposit chemistry and structure on physical and transport properties," *Abstracts of Papers of the American Chemical Society*, **211**, 112-FUEL.
12. Baxter, L. L. (1996) "Influence of Ash Deposit Chemistry and Structure On Physical and Transport-Properties," *Abstracts of Papers of the American Chemical Society*, **211**, 112-FUEL.
13. Baxter, L. L. (1997) "Ash," In *The Wiley Encyclopedia of Energy and the Environment*, Vol. 1 (Eds, Bisio, A. and Boots, S.) John Wiley & Sons, Inc., New York, pp. 198-213.
14. Baxter, L. L. (1998) "Influence of Ash Deposit Chemistry and Structure On Physical and Transport-Properties," *Fuel Processing Technology*, **56**, 81-88.
15. Baxter, L. L. (1999) "Application of Combustion Modeling to Boiler Problem Solving: Strengths and Weaknesses," In *CODE Kickoff Seminar*, Vol. 1 Tekes, Helsinki, Finland.
16. Baxter, L. L., Abbott, M. F. and Douglas, R. E. (1991) "Dependence of Elemental Ash Deposit Composition on Coal Ash Chemistry and Combustor Environment," In *Engineering Foundation Conference on Inorganic Transformations and Ash Deposition During*

- Combustion*(Ed, Benson, S. A.) The American Society of Mechanical Engineers, Palm Coast, Florida, pp. 679-698.
17. Baxter, L. L. and Chigier, N. (Eds.) (1996) *Advanced Technology Applications to Ash-Related Problems in Boilers*, Elsevier, New York.
 18. Baxter, L. L., Davis, K., Sinquefield, S., Huey, S., Lipkin, J., Shah, D., Ross, J. and Sclipa, G. (1996) "Combustion Aspects of the Reapplication of Energetic Materials as Fuels As a Viable Demil Technology," *Energy & Fuels*, .
 19. Baxter, L. L. and DeSollar, R. W. (1991) "Ash Deposition as a Function of Coal Type, Location in a Boiler, and Boiler Operating Conditions: Predictions Compared to Observations," In *International Conference on Environmental Control of Combustion Processes*Honolulu, HA.
 20. Baxter, L. L. and DeSollar, R. W. (1993) "A Mechanistic Description of Ash Deposition During Pulverized Coal Combustion: Predictions Compared to Observations," *Fuel*, **72**, 1411-1418.
 21. Baxter, L. L. and DeSollar, R. W. (Eds.) (1996) *Application of Advanced Technology to Ash-Related Problems in Boilers*, Plenum, New York.
 22. Baxter, L. L. and Dora, L. (1992) "The Combustion Behavior of a Blend of Eastern and Western Coals: Comparisons Between a Blend and Its Individual Components," *ASME Paper No. 92-JPGC-FACT-14*, .
 23. Baxter, L. L., Fletcher, T. H. and Ottesen, D. K. (1988) "Spectral Emittance Measurements of Coal Particles," *Energy & Fuels*, **2**, 423-430.
 24. Baxter, L. L., Gale, T., Sinquefield, S. and Sclipa, G. (1997) In *Developments in Thermochemical Biomass Conversion*, Vol. 2 (Eds, Bridgwater, A. V. and Boocock, D. G. B.) Blackie Academic and Professional, London, pp. 1247-1262.
 25. Baxter, L. L., Huey, S., Lipkin, J., Shah, D., Ross, J. and Sclipa, G. (1996) "Boiler Fuel as a Recycling Option for Energetic Materials," In *Fourth International Symposium on Special Topics in Chemical Propulsion*Stockholm, Sweden.
 26. Baxter, L. L. and Jenkins, B. M. (1995) "Laboratory Illustrations of the Transformations and Deposition of Inorganic Material in Biomass Boilers," *Abstracts of Papers of the American Chemical Society*, **210**, 85-FUEL.
 27. Baxter, L. L. and Jenkins, B. M. (1995) "Laboratory Illustrations of the Transformations and Deposition of Inorganic Material in Biomass Boilers," In *ACS National Meeting, Division of Fuel Chemistry*Chicago, IL.
 28. Baxter, L. L., Jenkins, B. M., Blander, M., Dayton, D. and Milne, T. A. (1996) "Equilibrium Considerations During Ash Deposition in Biomass Boilers," In *9th European Bioenergy Conference*, Vol. 2 (Eds, Chartier, P., Ferrero, G. L., Henius, U. M., Hultberg, S., Sachau, J. and Wiinblad, M.) Elsevier, Copenhagen, Denmark, pp. 1108-1113.
 29. Baxter, L. L., Jenkins, B. M., Gale, T., Sinquefield, S. and Sclipa, G. (1996) "Ash Deposit Chemistry and Structure Influences on Physical and Transport Properties," In *9th European Bioenergy Conference*, Vol. 1 (Eds, Chartier, P., Ferrero, G. L., Henius, U. M., Hultberg, S., Sachau, J. and Wiinblad, M.) Elsevier, Copenhagen, Denmark, pp. 198-203.
 30. Baxter, L. L., Jenkins, B. M., Miles, T. R., Jr., T. R. M., Milne, T., Dayton, D., Bryers, R. W. and Oden, L. L. (1996) "Inorganic Material Deposition in Biomass Boilers," In *9th European Bioenergy Conference*, Vol. 2 (Eds, Chartier, P., Ferrero, G. L., Henius, U. M., Hultberg, S., Sachau, J. and Wiinblad, M.) Elsevier, Copenhagen, Denmark, pp. 1114-1122.

31. Baxter, L. L., Lipkin, J., Ross, J. and Sclipa, G. (1996) "NO_x Formation During Combustion of Energetic Materials," In *Second International Conference on Combustion (ICOC '96): Conversion and Environmental Problems of Energetic Materials Peaceful Utilization of Energetic Materials* St. Petersburg, Russia.
32. Baxter, L. L., Miles, T. R., Jr., T. R. M., Jenkins, B. M., Milne, T., Dayton, D., Bryers, R. W. and Oden, L. L. (1996) "The Behavior of Inorganic Material in Biomass-Fired Power Boilers: Field and Laboratory Experiences," In *Engineering Foundation Conference on Industrial and Utility Use of Biomass* Snowbird, UT.
33. Baxter, L. L., Miles, T. R., Jr., T. R. M., Jenkins, B. M., Milne, T., Dayton, D., Bryers, R. W. and Oden, L. L. (1996) "An Overview of the Alkali Deposits Project: The Behavior of Inorganic Material in Biomass-Fired Power Boilers," In *Developments in Thermochemical Biomass Conversion* Banff, Canada.
34. Baxter, L. L., Miles, T. R., Jr., T. R. M., Jenkins, B. M., Milne, T., Dayton, D., Bryers, R. W. and Oden, L. L. (1997) In *Developments in Thermochemical Biomass Conversion*, Vol. 2 (Eds, Bridgwater, A. V. and Boocock, D. G. B.) Blackie Academic & Professional, London, pp. 1424-1444.
35. Baxter, L. L., Miles, T. R., Miles, T. R., Jr., Jenkins, B. M., Richards, G. R. and Oden, L. L. (1993) "Transformations and Deposition of Inorganic Material in Biomass Boilers," In *Second International Conference on Combustion Technologies for a Clean Environment*, Vol. 1 (Ed, Carvalho, M. G.) Commission of European Communities, Lisbon, Portugal, pp. Biomass II: 9-15.
36. Baxter, L. L., Miles, T. R., Thomas R. Miles, J., Jenkins, B. M., Dayton, D., Milne, T., Bryers, R. W. and Oden, L. L. (1996) "The Behavior of Inorganic Material in Biomass-Fired Power Boilers -- Field and Laboratory Experiences: Volume II of Alkali Deposits Found in Biomass Power Plants," Sandia National Laboratories; National Renewable Energy Laboratory, .
37. Baxter, L. L. and Mitchell, R. E. (1992) "The Release of Iron During the Combustion of Illinois No. 6 Coal," *Combustion and Flame*, **88**, 1-14.
38. Baxter, L. L., Mitchell, R. E. and Fletcher, T. H. (1997) "Release of Inorganic Material During Coal Devolatilization," *Combustion and Flame*, **108**, 494-502.
39. Baxter, L. L., Mitchell, R. E., Fletcher, T. H. and Hurt, R. H. (1996) "Nitrogen Release During Coal Combustion," *Energy & Fuels*, **10**, 188-196.
40. Baxter, L. L. and Nielsen, H. P. (1997) "The Effects of Fuel-bound Chlorine and Alkali on Corrosion Initiation," In *American Chemical Society Annual Meeting* Las Vegas, NV.
41. Baxter, L. L. and Nielsen, H. P. (1997) "The Effects of Fuel-Bound Chlorine and Alkali On Corrosion Initiation," *Abstracts of Papers of the American Chemical Society*, **214**, 44-FUEL.
42. Baxter, L. L., Richards, G. and Harb, J. (1994) "Application of Advanced Technology to Ash-Related Problems in Boilers," In *EPRI Conference on the Effects of Coal Quality on Power Plants* EPRI, Charleston, SC.
43. Baxter, L. L., Richards, G. H., Ottesen, D. K. and Harb, J. N. (1993) "In Situ, Real-time Characterization of Coal Ash Deposits Using Fourier Transform Infrared Emission Spectroscopy," *Energy & Fuels*, **7**, 755-760.
44. Baxter, L. L., Richards, G. H., Ottesen, D. K. and Harb, J. N. (1993) "In-Situ ; Real-Time Characterization of Coal Ash Deposits Using Fourier-Transform Infrared-Emission Spectroscopy," *Energy & Fuels*, **7**, 755-760.

45. Baxter, L. L. and Robinson, A. (1999) In *Biomass: A Growth Opportunity for Green Energy and Value-added Products*, Vol. 2 (Eds, Overend, R. P. and Chornet, E.) Elsevier Science, Ltd., Oxford, UK, pp. 1277-1284.
46. Baxter, L. L. and Robinson, A. (1999) "Key Issues When Cofiring Biomass with Coal in pc Boilers," In *Pittsburgh Coal Conference* Pittsburgh, PA.
47. Baxter, L. L., Robinson, A. L., Buckley, S. and Sclippa, G. (1997) "Combustion Research in Sandia's Multifuel Combustor," In *PETC Program Review Meeting* Pittsburgh, PA.
48. Baxter, L. L., Robinson, A. L., Buckley, S. G., Junker, H., Sclippa, G. and Widell, K. E. (1997) "Biomass-Coal Cofiring: Imperatives and Experimental Investigations," In *3rd Biomass Conference of the Americas* Montréal, Ontario, Canada.
49. Baxter, L. L., Robinson, A. L., Buckley, S. G., Shaddix, C. R., Lunden, M. and Hardesty, D. R. (1997) "Task 4: Development of Guidelines for Cofiring Biomass and Pulverized Coal," Sandia National Laboratories, .
50. Baxter, L. L., Rumminger, M., Lind, T., Tillman, D. and Hughes, E. (2000) "Cofiring Biomass in Coal Boilers: Pilot- and Utility-scale Experiences," In *Biomass for Energy and Industry: 1st World Conference and Technology Exhibition* Seville, Spain, pp. accepted.
51. Baxter, L. L., Shaddix, C. and Huey, S. (1996 (to be submitted)) "Heating Value as a Measure of Fuel Quality," *Fuel*, .
52. Baxter, L. L. and Smith, P. J. (1993) "Turbulent Dispersion of Particles : the Stp Model," *Energy & Fuels*, **7**, 852-859.
53. Baxter, L. L. and Smith, P. J. (1993) "Turbulent Dispersion of Particles: The STP Model," *Energy & Fuels*, **7**, 852-859.
54. Bernath, P., Sinquefield, S. A., Baxter, L. L., Sclippa, G., Rohlfing, C. M. and Barfield, M. (1998) "In situ analysis of ash deposits from black liquor combustion," *Vibrational Spectroscopy*, **16**, 95-103.
55. Bernath, P., Sinquefield, S. A., Baxter, L. L., Sclippa, G., Rohlfing, C. M. and Barfield, M. (1998) "In-Situ Analysis of Ash Deposits From Black Liquor Combustion," *Vibrational Spectroscopy*, **16**, 95-103.
56. Brewster, B. S., Baxter, L. L. and Smoot, L. D. (1988) "Treatment of Coal Devolatilization in Comprehensive Combustion Modeling," *Energy & Fuels*, **2**, 362-370.
57. Buckley, S. G., Lunden, M. M., Robinson, A. L., Allen, D. C., Sandoval, A., Grebenkov, A. J. and Baxter, L. L. (1998) "Fate of Sr and Cs in Biomass Combustion," *Environmental Science*, (submitted).
58. Buckley, S. G., Robinson, A. L. and Baxter, L. L. (1998) "Energetics to Energy: Combustion and Environmental Considerations Surrounding the Reapplication of Energetic Materials as Boiler Fuel," In *Twenty-Seventh Symposium (International) on Combustion* Combustion Institute, Boulder, CO.
59. Buckley, S. G., Sclippa, G. C. and Baxter, L. L. (1998) "Combustion Tests of Rocket Motor Washout Material: Part I — Focus on Air Toxics Formation Potential and Asbestos Remediation," Sandia National Laboratories, Livermore, CA.
60. Chaney, J., Baxter, L. and Mehta, A. (2000) "Fireside Coal Quality Impacts Predicted by Boiler Simulator," In *Effects of Coal Quality on Power Plants: Ash Problems, Management and Solutions* Park City, UT.

61. Fletcher, T. H., Baxter, L. L. and Ottesen, D. K. (1987) "Spectral Emission Characteristics of Size-Graded Coal Particles," *Abstracts of Papers of the American Chemical Society*, **194**, 4-FUEL.
62. Grebenkov, A., Iakoushev, A., Baxter, L., Allen, D., Junker, H. and Roed, J. (1997) "Energy Production from Contaminated Biomass: Progress of On-going Collaboration Projects," In *Engineering Foundation Conference on the Economic and Environmental Aspects of Coal Utilization* Santa Barbara, CA, pp. 635-643.
63. Gupta, R., Wall, T. F. and Baxter, L. L. (1997) "Thermal Conductivity of Coal Ash Deposits," In *Engineering Foundation Conference on the Impact of Mineral Impurities on Solid Fuel Combustion* (Eds, Gupta, R., Wall, T. F. and Baxter, L. L.) Plenum Press, Kona, HI, pp. 65-84.
64. Gupta, R. P., Wall, T. F. and Baxter, L. L. (Eds.) (1999) *Impact of Mineral Impurities in Solid Fuel Combustion*, Plenum Publishers, New York.
65. Jenkins, B. M., Baxter, L. L. and Miles, T. R. (1998) "Combustion Properties of Biomass," *Fuel Processing Technology*, **54**, 17-46.
66. Junker, H., Baxter, L. L., Robinson, A. L. and Widell, K. E. (1997) "Cofiring Biomass and Coal: Plant Comparisons and Experimental Investigation of Deposit Formation," In *Engineering Foundation Conference on the Impact of Mineral Impurities on Solid Fuel Combustion* Kona, HI.
67. Junker, H., Fogh, F., Baxter, L. and Robinson, A. (1998) "Co-firing Biomass and Coal: Experimental Investigations of Deposit Formation," In *10th European Conference and Technology Exhibition* Würzburg, Germany.
68. Kaufmann, H., Nussbaumer, T., Baxter, L. L. and Yang, N. (1998) "Mechanisms of Deposit Formation During Biomass Combustion," In *Biomass for Energy and Industry: 10th European Conference and Technology Exhibition* Würzburg, Germany.
69. Miles, T. R., Baxter, L. L., Bryers, R. W., Jenkins, B. M. and Oden, L. L. (1996) "Boiler Deposits From Firing Biomass Fuels," *Biomass & Bioenergy*, **10**, 125-138.
70. Mitchell, R. E., Hurt, R. H., Baxter, L. L. and Hardesty, D. R. (1992) "Compilation of Sandia coal char combustion data and kinetic analyses: milestone report," Sandia,
71. Nielsen, H. P., Baxter, L. L., Sclippa, G., Morey, C., Frandsen, F. and Dam-Hansen, K. (1998) "Deposition of Potassium Salt on Heat Transfer Surfaces in Straw-fired Boiler: A Pilot-Scale Study," *Fuel*, submitted.
72. Nielsen, H. P., Baxter, L. L., Sclippab, G., Morey, C., Frandsen, F. J. and Dam-Johansen, K. (2000) "Deposition of potassium salts on heat transfer surfaces in straw-fired boilers: a pilot-scale study," *Fuel*, **79**, 131-139.
73. Nielsen, H. P., Frandsen, F. J., Dam-Johansen, K. and Baxter, L. L. (1997) "Chlorine-Induced High-Temperature Corrosion of Superheater Tubes - a Literature Study," Technical University of Denmark, Lyngby, Denmark.
74. Nielsen, H. P., Frandsen, F. J., Dam-Johansen, K. and Baxter, L. L. (2000) "The Implications of Chlorine-Associated Corrosion on the Operation of Biomass-fired Boilers," *Progress in Energy and Combustion Science*, **26**, 283-298.
75. Ottesen, D. K., Baxter, L. L., Radziemski, L. J. and Burrows, J. F. (1991) "Laser Spark Emission-Spectroscopy For Insitu ; Real-Time Monitoring of Pulverized Coal Particle Composition," *Energy & Fuels*, **5**, 304-312.

76. Richards, G. H., Harb, J. N. and Baxter, L. L. (1995) "Investigation of Mechanisms for the Formation of Ash Deposits for Two Powder River Basin Coals," In *Application of Advanced Technology to Ash Related Problems in Boilers* (Ed, Baxter, L. L.) Plenum, Waterville Valley, New Hampshire.
77. Richards, G. H., Harb, J. N., Baxter, L. L., Bhattacharya, S., Bupta, R. P. and Wall, T. F. (1994) "Radiative Heat Transfer in PC-Fired Boilers — Development of the Absorptive/Reflective Character of Initial Ash Deposits on Walls," In *Twenty-Fifth Symposium (International) on Combustion* The Combustion Institute, Irvine, CA.
78. Robinson, A. and Baxter, L. (2000) "A Framework for Simulating the Effects of Sintering on Ash Deposit Thermal Conductivity," In *Effects of Coal Quality on Power Plants: Ash Problems, Management and Solutions* Park City, UT.
79. Robinson, A., Baxter, L. L., Freeman, M., James, R. and Dayton, D. (1998) "Issues Associated with Coal-Biomass Cofiring," In *Bioenergy '98* Madison, Wisconsin.
80. Robinson, A., Lunden, M., Shaddix, C. and Baxter, L. L. (1999) "Combustion Rates of Maple Wood Particles," In *First Joint Meeting of the US Sections of the Combustion Institute*, Vol. 1 George Washington University, Washington D.C., pp. 405-408.
81. Robinson, A. L., Baxter, L. L., Dayton, D., Freeman, M. and Goldberg, P. (1997) "Biomass-Coal Cofiring Experience among Three Laboratories," In *NYSEG Reveiw Meeting* Geneva, New York.
82. Robinson, A. L., Baxter, L. L., Sclipa, G., Junker, H., Widell, K. E., Dayton, D. C., Belle-Oudry, D., Freeman, M., Walbert, G. and Goldberg, P. (1997) "Fireside Considerations when Cofiring Biomass with Coal in PC Boilers," In *Engineering Foundation Conference on the Impact of Mineral Impurities on Solid Fuel Combustion* Kona, HI.
83. Robinson, A. L., Buckley, S. G. and Baxter, L. L. (1998) "In Situ Measurements of the Thermal Conductivity of Ash Deposits," In *Twenty-Seventh Symposium (International) on Combustion* Combustion Institute, Boulder, CO, pp. 1727-1735.
84. Robinson, A. L., Buckley, S. G. and Baxter, L. L. (2000) "Thermal Conductivity of Ash Deposits 1: Measurement Technique," *Energy & Fuels*, , submitted.
85. Robinson, A. L., Buckley, S. G., Lunden, M., Shaddix, C. and Baxter, L. L. (1998) "Combustion characteristics of biomass fuels," In *Western States Section of the Combustion Institute* Berkeley, CA.
86. Robinson, A. L., Buckley, S. G., Sclipa, G. and Baxter, L. L. (1997) "In Situ Measurements of the Thermal Conductivity of Ash Deposits formed in a Pilot-Scale Combustor," In *Engineering Foundation Conference on the Impact of Mineral Impurities on Solid Fuel Combustion* Kona, HI.
87. Robinson, A. L., Buckley, S. G., Yang, N. Y. C. and Baxter, L. L. (2000) "Thermal Conductivity of Ash Deposits 2: Effects of Sintering," *Energy & Fuels*, , submitted.
88. Robinson, A. L., Junker, H. and Baxter, L. L. (1997) "Ash Deposition and Pollutant Formation when Corfiring Biomass with Coal in PC Boilers," In *EPRI Coal Quality Conference* Kansas City, MO.
89. Robinson, A. L., Junker, H. and Baxter, L. L. (1997) "Pollutant Formation, Ash Deposition, and Fly Ash Properties When Cofiring Biomass and Coal," In *Engineering Foundation Conference on the Economic and Environmental Aspects of Coal Utilization* Santa Barbara, CA.

90. Robinson, A. L., Junker, H., Buckley, S. G., Sclipa, G. and Baxter, L. L. (1998) "Interactions between Coal and Biomass when Cofiring," In *Twenty-Seventh Symposium (International) on Combustion* Combustion Institute, Boulder, CO, pp. 1351-1359.
91. Sinqeifield, S. A., Baxter, L. L. and William J. Frederick, J. (1998) "An Experimental Study of the Mechanisms of Fine Particle Deposition in Kraft Recovery Boilers," In *1998 TAPPI International Chemical Recovery Conference*, Vol. 2 TAPPI Press, Tampa, FL, pp. 443-467.
92. Tassopoulos, M., Baxter, L. L. and Rosner, D. E. (1994 (in press)) "Comparison of Predicted and Measured Microstructure of Coal Ash Deposits," *AIChE Journal*, .
93. Wall, T. F., Baxter, L. L., Richards, G. and Harb, J. N. (1994) In *Coal-Blending and Switching of Low-Sulfur Western Coals*(Eds, Bryers, R. W. and Harding, N. S.) ASME, New York, pp. 453-463.
94. Wall, T. F., Bhattacharya, S. P., Baxter, L. L., Richards, G. and Harb, J. N. (1995) "The Character of Ash Deposits and the Thermal Performance of Furnaces," *Fuel Processing Technology*, **44**, 143-153.
95. Wall, T. F., Bhattacharya, S. P., Baxter, L. L., Young, B. C. and Grisanti, A. A. (1995) "Ash Deposit Properties and Radiative Transfer in Coal Fired Plant - Current Understanding and New Developments," In *Application of Advanced Technology to Ash Related Problems in Boilers*(Ed, Baxter, L. L.) Plenum, Waterville Valley, New Hampshire.
96. Wall, T. F., Bhattacharya, S. P., Zhang, D. K., Gupta, R. P. and He, X. (1993) "The Properties and Thermal Effects of Ash Deposits in Coal-Fired Furnaces," In *Engineering Foundation Conference on Ash Deposition during Coal Combustion*Solihull, UK, pp. to appear.
97. Yang, N. Y. C. and Baxter, L. L. (1991) "Instrument and Sample Preparation Considerations for Computer-Controlled Scanning Electron Microscopy (CCSEM) Analyses," In *Conference on Inorganic Transformations and Ash Deposition During Combustion*(Ed, Benson, S. A.) ASME, Palm Coast, Florida, pp. 191-206.

Appendix 5: Databases

Extensive tables of raw data for the suite of coals and coal blends examined in the course of this work are available from Sandia National Laboratories. If you would like to receive these data, please contact the principal investigator Dr. Larry L. Baxter (Tel. 925 294 2862) or the Sandia project manager Dr. Donald R. Hardesty (Tel. 925 294 2321).

The data tables are representative of the data collected during this research. They primarily represent coal, fly ash, and deposit characteristics for a variety of coals under a variety of conditions. In most cases, several replicated experiments were performed, in which case the statistics for the experiments are included here. The data include fuel characterizations. These include proximate analyses (which includes moisture), ultimate analyses (including ash), ash chemistry, chlorine, forms of sulfur, heating value, acid soluble alkali, fusion temperatures (oxidizing and reducing), and size distributions. The chemical fractionation and other advanced analyses are maintained in a separate database and are not summarized here. For each of the quantities measured in these analyses, the mean, standard deviation, number of replicated samples, coefficient of variation, and 95% and 99% confidence intervals are included.

A few comments regarding these data are in order. The data are computed directly from results provided by analytical laboratories. As part of our quality control standards, we do not alter the data from the laboratories in the database. However, for reasons discussed earlier in this report, we do not believe the data are presented here in an optimal manner. Specifically, the ultimate analysis results should include chlorine and should be done on an ash-free basis. The ash should be included with the proximate analysis results. This is how the data are presented in the summary tables in Appendix 1, but it is not generally the way they are reported from analytical laboratories.

Analyses of products of combustion follow those of fuel characterization. For example, analyses of fly ash samples collected at various stages of combustion are included. These data include overall mass loss, elemental loss of the organic and inorganic fractions, etc. The data are first summarized, and then presented with their statistics (mean, standard deviation, effective number of replicated samples, coefficient of variation, and 95% and 99% confidence intervals). Data on deposit compositions, deposition rates, thermal conductivities, emissivities, etc. are maintained in experiment-specific files and are not included here.

Data are available for the following coals:

San Miguel Lignite

Beulah Lignite

Eagle Butte

Roland

Wyodak

Decker

Hanna Basin

Belle Ayr

Kentucky #11

Illinois #6 (1)

Kentucky #9

Illinois #6 (2)

Blind Canyon

Eastern Kentucky

Pittsburgh #8 (2)

Massey Spruce

Upper Freeport

Pittsburgh #8 (3)

Pittsburgh #8 (1)

Pocahontas #3

Eagle Butte/Kentucky#9 Blend

Roland/Illinois #6 (2) Blend

Pittsburgh/Decker Blend

Eastern Blend

INITIAL DISTRIBUTION

Dr. Donald Aitken
Union of Concerned Scientists
2625 Alcatraz Ave., Suite 505
Berkeley, CA 94705

Dr. Suresh P. Babu
Institute of Gas Technology
1700 South Mount Prospect Road
Des Plaines, Illinois 60018-1804

Mr. Phillip Badger
Tennessee Valley Authority
SE Regional Biomass Program
PO Box 1010
Muscle Shoals, AL 35662-1010

Dr. Richard Bain, Manager
Biomass Power Program
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393

Dr. Steve Benson
UND Energy and Environ. Res. Center
P.O. Box 9018
Grand Forks, ND 58202-9018

Mr. William M. Burnett
Senior Vice President
Technology Development
Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, IL 60631

Mr. William H. Carlson
Wheelabrator Environmental Systems
20811 Industry Road
Anderson, CA 96007

Mr. Kevin Craig
Biomass Power Program
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393

Dr. Raymond Costello
Manager
Biomass Power Program, EE-13
U.S. DOE
1000 Independence Avenue, SW
Washington, D.C. 20585

Dr. Stefan Czernik
Research Chemist
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393

Professor John W. Daily
Univ. of Colorado at Boulder
Mechanical Engineering Dept.
Boulder, CO 80309-0427

Dr. Kevin Davis
Reaction Engineering International
77 West 200 South, Suite 210
Salt Lake City, UT 84101

Dr. David Dayton
Staff Thermochemical Scientist
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393

Dr. Thomas H. Dunning, Jr., Manager
Molecular Sciences Research Center
Pacific Northwest National Laboratories
P. O. Box 999, MS K2-20
Richland, WA 99352

Dr. Robert Evans
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393

Dr. Robert B. Finkelman
U.S. Geological Survey
956 National Center
Reston, VA 22092-0000

Prof. Rick Flagan
California Institute of Technology
Environmental Engineering Dept.
Mailcode 138-78
Pasadena, CA 91125

Prof. Thomas Fletcher
Department of Chemical Engineering 350
Clyde Building
Brigham Young University
Provo, UT 84602

Dr. Patrick F. Flynn
Vice President, Research & Technology
Cummins Engine Company
Mail Code 50181, Box 3005
Columbus, IN 47202-3005

Dr. W. James Frederick Jr.
Institute of Paper Science And Technology
500 - 10th Street NW
Atlanta, GA 30318

Dr. Robert Gemmer
Program Manager
U.S. Department of Energy
Energy Efficiency and Renewable Energy
Office of Industrial Technologies
1000 Independence Avenue, SW
Washington, DC 20585-0121

Mr. Philip Goldberg (10)
US DOE / NETL
922-342
626 Cochran Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

Dr. J. Peter Gorog
Research and Development
Pulp, Paper and Packaging
Weyerhaeuser Company
WTC 2H22
Tacoma, WA 98477

Mr. Jeff Graef
W Regional Biomass Energy Program
Nebraska Energy Office
1200 N Street Suite 110
Lincoln, NE 68509-5085

Mr. Richard Handley
NE Regional Biomass Energy Program
Coneg Policy Research Center Inc.
400 N Capital St NW Suite 382
Washington, DC 20001

Professor Ronald K. Hanson, Chair
Department of Mechanical Engineering
Stanford University
Stanford, CA 94305

Dr. Mike Heap
Reaction Engineering International
77 West 200 South Suite 210
Salt Lake City, UT 84101

Dr. Donald J. Holve
Process Metrix, LLC
2110 Omega Rd., Ste. D
San Ramon, CA 94583

Dr. Evan Hughes
Manager, Renewable Fuels
Electric Power Research Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94303

Prof. Robert Hurt
Division of Engineering
Brown University
Box D
Providence, RI 02912

Dr. Ari Huttunen
EPRI
Coal Combustion & Renewables
Energy Conversion
3412 Hillview Ave.
Palo Alto, CA 94304-1395

Professor Bryan M Jenkins
University of California, Davis
Biological and Ag. Eng. Dpt.
Davis, CA 95616-5294

Dr. Andrew K. Jones
International Paper
Manufacturing Technology Center
6285 Tri-Ridge Blvd.
Loveland, OH 45140-7910

Mr. Frederick Kuzel
Council Great Lakes Governors
Great Lakes Regional Biomass Program
35 E Wacker Drive Suite 1850
Chicago, IL 60601

Dr. Steve Londerville
Director of Research & Development
The Coen Company, Inc.
1510 Rollins Road
Burlingame, CA 94010

Professor Gregory J. McRae
Department of Chemical Engineering
Massachusetts Institute of Technology
Room 66-372
77 Massachusetts Avenue
Cambridge, MA 02139-4307

Dr. Arun Mehta
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304-1395

Mr. Thomas R. Miles
Consulting Design Engineer
5475 SW Arrowwood Lane
Portland, OR 97225

Professor Reginald E. Mitchell
Dept. of Mechanical Engineering
Stanford University
HTGL 520C,
Stanford, CA 94305-3032

Dr. Gregory P. Morris
Future Resources Associates, Inc.
2039 Shattuck Ave. Suite 402
Berkeley, CA 94704

Dr. Ralph P. Overend
National Renewable Energy Lab
1617 Cole Boulevard
Golden, CO 80401-3393

Mr. Pekka Pakkala
Embassy of Finland
Technology Center
3301 Massachusetts Ave., NW
Washington, DC 20008

Dr. Robert R. Romanosky (10)
Power Systems Advanced Research
National Energy Technology Laboratory
3610 Collins Ferry Road
PO Box 880
Morgantown, WV 26507-0880

Dr. Thomas Reed
Colorado School of Mines
1810 Smith Road
Golden, CO 80401

Prof. Allen Robinson
Scalfe Hall 303
Dept. of Mechanical Engineering
Carnegie Mellon University
5000 Forbes Ave.
Pittsburgh, PA 15213-3890

Ms. Valri Robinson
Office of Industrial Technologies
DOE EE-22 Room 5F-035
Washington D.C. 20585

Mr. Robert Roscoe
Weyerhaeuser
Technology Center
Federal Way, WA 98003

Prof. Daniel E. Rosner
Yale University
Mason Laboratory
New Haven, CT 6520

Prof. Adel Sarofim
Univ. of Utah & MIT
Dept. of Chemical Eng.
Salt Lake City, UT 84112

Dr. Daniel J. Seery
Senior Program Manager
Environmental Science
United Technologies Research Center
East Hartford, CT 06108

Dr. David G. Sloan
ABB-Combustion Engineering, Inc.
2000 Day Hill Road
Windsor, CT 6095

Prof. Philip Smith
Dept. of Chemical and Fuels Engineering
2250 Merrill Engineering Building
Salt Lake City, UT 84112

Prof. L. Douglas Smoot
Department of Chemical Engineering
435T Crabtree Technology Building
Brigham Young University
Provo, Utah 84602

Mr. Scott M. Smouse
NETL
P.O. Box 10940
Pittsburgh, PA 15236-0940

Dr. Peter Solomon
Advanced Fuel Research
P.O. Box 18343
East Hartford, CT 6108

Dr. John Stringer
Executive Technical Fellow
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94303

Dr. Chris Verrill
Research Chemical Engineer
Westvaco Corporation
PO Box 118005
Charleston, SC 29423-8005

Mr. Dave Waltzman
US Department of Energy
Denver Regional Support Office
1617 Cole Boulevard
Golden, CO 80401

Mr. Larry Watson
Chevron Research & Technology
100 Chevron Way
Richmond, CA 94802

Prof. Jost O. L. Wendt
Dept. of Chemical Engineering
University of Arizona
Tucson, AZ 85721

Dr. Rick Wessel
McDermott Technologies Inc.
1562 Beeson St.
Alliance, OH 44601

Prof. Judy Wornat
Dept. of Mech. & Aerospace Engr.
Princeton University
Princeton, NJ 08544-5263

Mr. Warren Zurn
DOE Atlanta Support Office
730 Peachtree Street NE Suite 876
Atlanta, GA 30308

Mr. Francisco Domingues Alves de Sousa
Instituto de Pesquisas Tecnologicas do
Estado de Sao Paulo - IPT
Cidade Universitaria - CEP 05508-901
Sao Paulo-SP, Brazil

Dr. Javier Ballester
University of Zaragoza
María Zayas, 12, 5º A
50015-Zaragoza
Spain

Professor Tony Bridgwater
Chem. Eng. And Appl. Chem.
Aston University
Aston Triangle
Birmingham B4 7ET
United Kingdom

Dr. Mark Douglas
A/Group Leader, CO2 Abatement
CANMET Energy Technology Center
1 Haanel Drive
Nepean, ON K1A 1M1
Canada

Mr. John Gifford
Project Leader, Energy
Forest Research
Private Bag 3020
Rotorua
New Zealand

Dr. Alexandre J. Grebenkov
Head of Laboratory
Institute of Power Engineering Problems
Sonsy, 220109
Minsk Belarus

Dr. Steven Gust
Fortum
Technology Centre
P.O. Box 310
FIN-06101
Porvoo, Finland

Prof. Hermann Hofbauer
Institut für Verfahrenstechnik
Brennstofftechnik und Umwelttechnik
Getreidemarkt 9
A-1060 Wien
Austria

Dr. Patrick Hughes
Natural Resources – Canada
CANMET
1 Haanel Drive
Nepean, Ontario
Canada K1A-1M1

Prof. Mikko Hupa
Åbo Akademi University
Lemminkäisenkatu 14-18 B
FIN-20520 Åbo/Turku
Finland

Prof. Johan Hustad
SINTEF Thermal Energy and
Fluid Machinery
7034 Trondheim
Norway

Dr. Jun Inumaru
Central Research Institute
of Elec. Power Ind.
2-6-1 Nagasaka, YOKOSUKA 240-01
Japan

Dr. Tommy Jacobon
Fortum Power and Heat Oy
POB 20, 00048
FORTUM, Finland

Mr. Henrik Houmann Jakobsen
DK-Teknik
Gladsaxe Mollevej 15
DK-2860 Soborg
Denmark

Mr. Kauko Janka
Kværner Pulping Oy
Kelloportinkatu 1 D
Box 109
Tampere, FIN+33101
Finland

Dr. Helle Junker
Elsamprojekt A/S Power Station
Engineering
53 Kraftvaerksvej
DK-7000 Fredericia Denmark

Dr. Jaap Koppejan
TNO Institute of Environmental Sciences
Dept. of Thermal Conversion Technology
P.O. Box 342
7300 AH Apeldoorn
The Netherlands

Dr. Terttaliisa Lind
VTT Chemical Technology
PO Box 1401, FIN-02044 VTT
Biologinkuja 7, Espoo
Finland

Dr. Alexander A. Mikhalevich
Academy of Sciences, Belarus
Institute of Power Engineering Problems
IPEP, SOSNY
Russia

Dr. Thomas Nussbaumer
Verenum
Langmauerstrasse 109
CH-8006 Zurich
Switzerland

Dr. Ingwald Obernberger
Institute of Chemical Engineering
Technical University of Graz
Inffeldgasse 25
A-8010 Graz
Austria

Dr. Aksel Olsen
Risoe National Laboratory
Optics & Fluid Dynamics Dept.
P.O. Box 49 – Bldg. OFD-201
Frederiksborgvej 399
DK-400 Roskilde
Denmark

Mr. Heikki Oravainen
VTT Energy
Fuels and Combustion
P.O. Box 1603
FIN-40101-Jyvaskyla
Finland

Dr. Niranjana Patel
ETSU, B156
Harwell
OXON OX11 0RA
United Kingdom

Prof. Dimos Poulidakos
Swiss Federal Institute of Technology
Institute for Energy Technology
ETH-Zentrum
CH-8092 Zürich
Switzerland

Mr. Erik Rensfelt
TPS Termiska Processer AB
Studsvik S-611 82 Nyköping
Sweden

Mr. Joe Robert
CANMET
580 Booth Street-13th Floor
Ottawa, Ontario K1A 0E4
Canada

Dr. Yves Schenkel
Chef de travaux-Section Biomass
Head-Biomass Unit
CRA-Département Génie rural
Chee de Namur, 146
B-5030 Gembloux
Belgium

Ann Segerborg-Fick
Rue de la Loi 200
1000 Brussels
Belgium

Dr. Oyvind Skreiberg
Institutt for Termisk Energi og Vannkraft
Fakultet for Maskinteknikk
NTNU, 7491 Trondheim
Norway

Dr. Yrjo Solantausta
VTT Energy
PO Box 1610
FIN-0244 VTT, ESPOO
Finland

Mr. Frans Sulilatu
TNO-MEP, Dep. Combustion Conversion
P.O. Box 342
NL-7300 AH Apeldoorn
Netherlands

Professor Honghi Tran
Department of Chemical Engineering &
Applied Chemistry
University of Toronto
200 College Street
Toronto, Canada M4S 1A4

Claes Tullin
Energiteknik/Energy Technology
SP, Sveriges Provnings-och
Forskningsinsstitut
Swedish National Testing and Research
Institute Box 857 S-501 15 Boras
Sweden

Mr. John Tustin
Forest Research
Private Bag 3020
Rotorua
New Zealand

Mr. Sjaak van Loo
TNO, PO Box 342
NL-7300 AH Apeldoorn
The Netherlands

Prof. Terry Wall
University of Newcastle
Rankin Drive
Newcastle 2308
NSW
Australia

Prof. Franz Winter
Technische Universität Wien
Institut fuer Verfahrenstechnik
A-1060 Wien
Austria

SANDIA DISTRIBUTION

MS0750 D. J. Borns, 6116

MS0741 S. G. Varnado, 6200

MS0703 T. R. Mancini, 6216

MS9001 M.E. John, 8000

Attn: 8100 J. Vitko
8400 D. Hensen
8700 M. Dyer
8362 K. Washington

MS9105 B. Wu, 8119

MS9054 W. J. McLean, 8300

Attn: 8350 F. Tully
8351 L. Rahn
8356 R. Gallagher
8360 R. Carling
8362 J. Keller
8363 T. Bramlette

MS9052 L. L. Baxter, 8361 (10)

MS9052 D. R. Hardesty, 8361(20)

MS9052 G. Sclipa, 8361

MS9052 C. R. Shaddix, 8361

MS9051 A. E. Lutz, 8362

MS9053 P. Walsh, 8366

MS9403 J. Wang, 8723

Attn: N. Yang

MS9042 M. Perra, 8728

Attn: S. Griffiths
W. Houf
R. Larson
R. Nilson

MS9018 Central Technical Files,
8940-2 (3)

MS0899 Technical Library, 4916

MS9021 Technical Communications
Department, 8815/Technical Library,
MS 0899, 4916

MS9021 Technical Communications
Department, 8815 for DOE/OSTI