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TRANSFORMATIONS OF INORGANIC COAL
CONSTITUENTS IN COMBUSTION SYSTEMS

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TABLE OF CONTENTS

<u>Section No.</u>		<u>Page</u>
1.	EXECUTIVE SUMMARY	1-1
2.	INTRODUCTION AND OVERVIEW OF PROGRAM TASKS	2-1
3.	TASK 5 - FUNDAMENTAL STUDIES OF MINERAL MATTER VAPORIZATION AND RESIDUAL ASH FORMATION	3-1
3.1	Char Combustion Modeling	3-3
3.1.1	Previous Models	3-3
3.1.2	This Model	3-6
3.1.3	Comparison of Model Results to Data from Timothy et al., 1982	3-29
3.1.4	References for Section 3.1	3-31
3.2	Simulation of Residual Ash Formation with a Continuum Model	3-33
3.2.1	Model Assumptions	3-33
3.2.2	Model Formulation	3-36
3.2.3	Parameter for Ash Growth	3-39
3.2.4	Scaling of the Ash Particle Size Distribution	3-53
3.2.5	Planar Study of the Model	3-56
3.2.6	Summary	3-74
3.2.7	References for Section 3.2	3-78
4.	TASK 8 - ENGINEERING MODEL DEVELOPMENT	4-1
4.1	Introduction	4-3
4.2	Initial Coal Particle Size Distribution	4-3
4.3	Limited Coalescence Option	4-3
4.4	Distribution of Small Mineral Particles on Small Coal Particles	4-3
4.5	Model Predictions of Ash Size and Composition Obtained from Combustion of Illinois #6 Coal	4-9

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
3-1	Temperature Calculation Algorithm	3-16
3-2	Effect of Oxygen Disassociation on Thermal Conductivity	3-22
3-3	Effect of the O_2/C Ratio on the Predicted Particle Temperature	3-25
3-4	Temperature versus Oxygen Concentration, Comparison to Timothy et al. (1982)	3-30
3-5	Illustration of a Formation on a Flyash Particle	3-41
3-6	Illustration of the Coalescence Length Scale	3-45
3-7	Illustration of the Coalescence Length Scale for Spherical Char Configuration	3-50
3-8	Growth of Average Surface Ash Size r_{ash} with the Reaction Depth z	3-59
3-9	Growth of Average Surface Ash Size Rescaled with Mineral Inclusion Size (r_{ash}/r_m) with the Reaction Depth Rescaled with the Separation Length ($/L_s$)	3-60
3-10	Comparison of Average Surface Ash Sizes from Simulation with Those Analytically Predicted	3-61
3-11	Growth of Mass Mean Size of the Separated Ash r_{ash} with the Reaction Depth z	3-62
3-12	Comparison of the Growth of the Mass Mean Size of Separated Ash with That of the Surface Ash	3-63
3-13	Final Ash Number Distributions for Simulations on Planar Char Configuration	3-64
3-14	Scaling of Mass Distributions of Final Ash	3-66
3-15	Growth of the Average Surface Ash Radius Obtained from the Computer Simulation of a Typical Bituminous Coal	3-67

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
3-16	Surface Ash Particle Size Distributions Obtained from the Simulation of a Typical Bituminous Coal of 8 Vol% Mineral Content	3-68
3-17	Growth of Surface Ash with Conversion on a Non-Porous Char	3070
3-18	Effect of Mineral Inclusions on Ash Growth Behavior	3-73
3-19	Correlation Between the Ash Growth Number and the Mass Mean Radii of Separated and Surface Ash	3-75
3-20	Ash Mass Distributions from Simulations in Spherical Configurations	3-76
4-1	Ash Particle Size Distributions, as Measured by CCSEM, Generated by Combustion of Illinois #6 Coal at PSIT and UA, and Compared to Model Predictions	4-12
4-2	Comparison of Ash Composition Distribution for Illinois #6 Coal	4-13
4-3	Calcium-Rich Particle Size Distribution (Illinois #6)	4-14
4-4	Calcium Interactions for Illinois #6 Coal	4-15
4-5	Iron Interactions for Illinois #6 Coal	4-16

LIST OF TABLES

<u>Table</u>		<u>Page</u>
3-1	Model Results as a Function of Diameter for 10 Percent Oxygen	3-27
3-2	Model Results as a Function of Diameter for 80 Percent Oxygen	3-27
3-3	Summary of Model Results	3-28
3-4	Input Conditions for Computer Simulation Runs	3-57
4-1	Simulated Coal and Mineral Particle Distributions for Illinois #6	4-5
4-2	Simulated Coal and Mineral Particle Distributions for San Miguel Lignite	4-6
4-3	Measured and Derived Mineral Size Distributions for Illinois #6	4-9
4-4	Coalescence Parameter (mineral inclusion size for which coalescence occurs, in μm)	4-10
4-5	Ash Size and Composition Distribution (Area %)	4-11
4-6	Size Distribution (Number %) of Fe-Rich Particles: Model Calculations and PSIT Ash Data	4-16

SECTION 1

EXECUTIVE SUMMARY

1. EXECUTIVE SUMMARY

The technical objectives of this project are:

- a. To: 1) define the partitioning of inorganic constituents associated with raw coal particles among products (including vapors, aerosols, and residual char/ash particles) formed under conditions representative of pulverized coal flames as a function of the specific (intrinsic and extrinsic) characteristics of the raw coal and the environment in which the transformations occur; and 2) characterize the resultant spectrum of products in detail.
- b. To elucidate and quantify the fundamental processes (involving basic principles of physics, chemistry, thermodynamics) by which transformations of the inorganic constituents occur.
- c. To develop, based on the information required in a. and b. above, a tractable "process" model capable of predicting the significant features of the transformation process, most importantly, the nature and distribution of products.

The contract approach and description of each task is included in Section 2 of this report. This report summarizes work accomplished during the sixteenth quarter of this project. During this time, emphasis was placed on modeling activities in several areas. Experimental activities are expected to increase during the coming months as the new coals selected for this portion of the program arrive in the various laboratories.

The work discussed herein highlights recent accomplishments: at the Massachusetts Institute of Technology (MIT), in modeling synthetic char particle combustion times and temperatures with allowance for oxygen dissociation in the char boundary layer; at MIT, in developing a continuum model for residual ash formation and char fragmentation, permitting a more detailed time-resolved study of ash coalescence within a burning char particle; and at PSI Technology Company (PSIT), in continuing development of the engineering model for ash particle formation.

In Section 3, a description of a recently completed char combustion model developed at MIT is presented. This pseudo-steady state model incorporates intrinsic carbon reaction kinetics, important in this system for particles $< 80 \mu\text{m}$ in size at temperatures $< 2200 \text{ K}$, allows for the partial oxidation of CO to CO_2 in the char boundary layer, and unlike all previous models, allows for the dissociation of oxygen within the boundary layer, increasing the thermal conductivity of that region. Oxygen dissociation effects on the gas thermal conductivity can be significant - results in this section demonstrate that a five-fold increase in thermal conductivity for 80 percent O_2 at 3200 K arises from dissociation. Incorporation of these phenomena into the char combustion model resulted in a highly accurate prediction of

literature combustion temperatures previously measured in this system. Plausible explanations for reported differences in bituminous and lignite combustion temperature were also derived from the calculations presented in this section. For coals burning as a cenosphere, results suggest that a time/volume weighted average, roughly corresponding to the maximum particle temperature, is the correct average, as particle diameter does not change significantly during most of burnout. For low-rank coals burning as shrinking spheres, a time-weighted average over the first 99.95 percent of char combustion appears more appropriate.

Also in Section 3, the development of a Monte Carlo model to simulate flyash particle growth on the char surface in continuum space is presented. In prior reports, results from a percolation simulation of flyash formation were presented. That model (percolation) provided insight into char fragmentation patterns, but yielded little information on the competing process of ash coalescence on the char surface. This complementary Monte Carlo simulation (continuum model) was therefore developed as a necessary means of following the dynamics of the coalescence process more closely. In the continuum model, oxidation is allowed *within* macropores (i.e., those pores $> 0.1 \mu\text{m}$, having an effectiveness factor of 0.9). Ash separation from the char occurs when an ash particle on the receding char surface encounters underlying pore space. By utilizing a semi-infinite planar configuration, ash formation in swelling chars can be simulated; a spherical configuration is used for ash formation in non-swelling chars. Based upon these efforts, an ash parameter can be developed which relates coalescence length scale to fragmentation length scale, leading to a closed form expression for the average number of coalescence events occurring before an ash particle is separated by fragmentation. Simulation results indicate an increasingly broad ash particle size distribution results when this parameter increases. Results also suggest that for highly swelling coals, one ash particle per mineral inclusion may be a good approximation to the size for the residual ash formed within the char particles.

In Section 4, recent efforts in development of an engineering model for ash size and chemical composition are presented. Progress on code development was made in three areas: (1) implementation of a higher resolution input coal size distribution, (2) more flexible treatment of coalescence of individual minerals, and (3) a probabilistic treatment of distribution of small minerals onto the smallest coal particles. Results generated with the latest version of the code and their comparison with experimental data for Illinois #6 coal are presented.

SECTION 2

INTRODUCTION AND OVERVIEW OF PROGRAM TASKS

2. INTRODUCTION AND OVERVIEW OF PROGRAM TASKS

This project consists of an integrated series of experimental and modeling tasks performed by PSI Technology Company (PSIT) and three subcontractors (identified below) to achieve the project objectives. Additional work is to be conducted jointly with the University of North Dakota Energy and Environmental Research Center (UND EERC) and the State Electricity Commission of Victoria, Australia (SECV) through cooperative agreements. Important elements of this work include coal and ash characterization using advanced analytical techniques, testing in small scale furnaces, testing in moderate to large-pilot scale units, adaptation of fundamental submodels developed previously to beneficiated coal systems, and integration of these submodels and experimental findings into an engineering model used to predict ash particle composition and size distributions. A breakdown of the work to be performed in each task is presented below.

Task 1 - Program Planning, Management, Reporting, and Peer Review

This task, to be performed by PSIT, consists of: (1) preparation and annual updating of a Program Plan; (2) overall coordination, management, and integration of the subcontracts and project results; (3) preparation of project monthly reports; (4) integration and final preparation of project quarterly reports; and (5) conduct of semi-annual peer review and project coordination meetings of the project Principal Investigators.

Task 2 - Coal Selection, Preparation, and Characterization

This task will be performed by PSIT using the guidelines for mineralogy-based coal selection developed by Foster Wheeler Development Corporation (FWDC) during the first phase of this project. Five parent coals plus one beneficiated sample of each coal with an optional two sets of additional coals will be selected to permit an experimental determination of beneficiation related variables on inorganic transformations during combustion. Emphasis will be placed on obtaining both eastern and western coals, cleaned with currently accepted and advanced beneficiation strategies. Coals will be acquired by PSIT, pulverized as necessary by an independent contractor on a purchase order basis, and shipped to the various investigators.

Task 3 - Advanced Techniques for Coal and Mineral Characterization

The University of Kentucky (UK) will apply advanced analytical techniques to determine the form, size, and associations of the coal minerals and the resulting ash particles. Work to be performed in this broad area can be broken down into three Subtasks. Under Subtask 3.1, UK will work with other research groups to make improvements in the computer controlled scanning electron microscopy (CCSEM) technique. This will include software improvements to permit the CCSEM to distinguish between extraneous and included mineral matter in an automated fashion. Under Subtask 3.2, UK will apply CCSEM, Mossbauer spectroscopy, x-ray absorption fine structure analysis (XAFS), and scanning transmission electron microscopy (STEM) to analyze the mineral forms in the parent coals

and the resulting ash products. X-ray diffraction will also be used as needed for mineral analysis. Under Subtask 3.3, UK will develop an in-situ XAFS capability at the Brookhaven National Laboratories (BNL) Light Source, to be used to determine the associations of inorganic species in ash particles and initial sticky particle layers without the complications posed by quenching and extractive sampling.

Task 4 - Fundamental Studies of Selected Ash Vaporization, Nucleation, Condensation, and Coagulation Phenomena

Task 4, to be performed by PSIT, involves thermochemical modeling of the inorganic species expected to be present in the parent coal particles, the beneficiated coal particles, and the final ash particles at various combustion conditions.

Task 5 - Fundamental Studies of Mineral Matter Vaporization and Residual Ash Formation

Experimental and modeling studies are to be conducted at the Massachusetts Institute of Technology (MIT) on two Subtasks. Under Subtask 5.1, drop tube furnace combustion experiments will be conducted with parent coals, beneficiated coals, and model chars to assess the importance of the various mechanisms which control residual ash formation. Emphasis will be placed on the expected increasing importance of char fragmentation in shaping the distribution, both experimentally and through adaptation of the percolative fragmentation model developed in the first phase of this project. In Subtask 5.2, the extent of vaporization of inorganic species contained in the parent and beneficiated coals will be examined experimentally. Vaporization models developed previously will be utilized to interpret results from beneficiated systems.

Task 6 - Pulverized Coal Combustion Studies of Ash Enrichment by Volatiles

The objectives of this task, to be performed at the University of Arizona (UA) self-sustained reactor facility, are to determine the different fume amounts, compositions, and structures resulting from various beneficiation processes. Mechanistic descriptions of the size and surface composition of the submicron fume formed during combustion will be developed. Testing will occur on selected parent and cleaned coals, chosen subsequent to initial screening in the PSIT reactor facility. As part of this effort, the size of the residual ash particles will be measured in-situ using an optical single particle measuring instrument provided by PSIT. A model capable of describing the general ash particle size distribution including the effects of fume formation and char fragmentation will also be developed.

Task 7 - Idealized Combustion Determination of Ash Particle Formation and Surface Stickiness

In this task, PSIT will employ an idealized combustion system to determine ash particle size and composition distributions for comparison with results obtained at MIT and UA. Emphasis will be placed on quantifying the amount of fume, and the amount and chemical composition of ash generated from the various beneficiated coals. Particle

stickiness as it pertains to inertial impaction and thermophoretic deposition will be addressed. Particle size will be analyzed by several means as part of the task, including CCSEM, laser diffraction, and aerodynamic impaction. In addition, the combustor portion of an in-situ XAFS cell will be designed and constructed. Experiments utilizing this cell will be conducted with UK and BNL at the BNL Light Source to determine ash composition and sticky particle composition in-situ.

Task 8 - Model Development and Integration

In this task, PSIT will synthesize the mineral redistribution, char particle fragmentation, and mineral transformation models developed under the various tasks into an overall ash formation model. The result of this synthesis will be an engineering model capable of describing the size and, more importantly, the chemical composition of residual ash generated during pulverized coal combustion and the quantity and composition of the ash fume. The information provided by this model will then be used to assess the benefits of coal cleaning through a parametric study of ash properties resulting from selective mineral removal.

SECTION 3

TASK 5 - FUNDAMENTAL STUDIES OF MINERAL MATTER VAPORIZATION AND RESIDUAL ASH FORMATION

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3. TASK 5 - FUNDAMENTAL STUDIES OF MINERAL MATTER VAPORIZATION AND RESIDUAL ASH FORMATION

During the past quarter, modeling efforts were carried out to a) predict synthetic char combustion temperatures for vaporization data analysis, and b) examine the influence of coalescence on fragmentation patterns and residual ash formation. Efforts in both areas are described in the following pages.

3.1 Char Combustion Modeling

In order to interpret the vaporization data reported in previous quarterly reports, char combustion temperatures and burning time were calculated. The assumptions and method of calculation are discussed in this quarterly report.

3.1.1 Previous Models

In order to develop the most accurate char combustion model possible, previous modeling efforts were first reviewed.

Basic Assumptions

During the past 65 years, char burnout during pulverized coal combustion has been modeled by a number of researchers such as Nusselt, 1924, Spalding, 1953, Field et al., 1967, Ayling and Smith, 1972, Timothy et al., 1982, and Waters et al., 1988. Each of these researchers has made a similar set of readily justifiable assumptions in relation to the following set of basic questions: Can the energy and mass transport be modeled as a continuum? Do the particles influence one another? Is convection important? Is the particle isothermal? What chemical reactions must be considered? Each of these assumptions will be discussed briefly with respect to the experiments performed at MIT in this project.

Can the energy and mass transport be modeled as a continuum? A simple calculation shows that the mean free path of the gas is never significantly greater than $1\text{ }\mu\text{m}$ under the experimental conditions explored. Thus, as long as the char particle is $10\text{ }\mu\text{m}$ or greater, the transport can be modeled as a continuum.

Do the particles influence one another? In the laminar, entrained-flow reactor, each coal particle was injected along the same path down the centerline of the reactor at approximately 60 cm/s. At the maximum feed rate used (0.02 g/min) the particles were spaced over 10 diameters apart. Given the boundary layer surrounding the particles is generally considered to be 1 to 2 diameters, the particles were assumed to have no influence on one another.

Is convection important? The maximum settling velocity, and hence the maximum velocity of the particles relative to the gas, for the experimental conditions of this thesis was always less than 40 cm/s. Using that velocity, the Sherwood and Nusselt numbers for a

100 μm sphere in air at 1650 K are virtually 2 (Satterfield, 1981), therefore, forced convection may be ignored and the char particles may be assumed to be suspended in a stagnant gas of infinite extent.

Is the particle isothermal? If the characteristic time for conduction is defined as the energy transferred to the char particle/initial heating rate, then the characteristic conduction time for a 100 μm char particle is approximately 0.001s. The burn time for a 100 μm char particle is known to be between 1 and 0.1s. Thus, the particle can be assumed to be isothermal, and char combustion can be modeled assuming the char achieves a steady state temperature much more rapidly than the diameter changes. This conclusion was verified experimentally by Timothy et al., 1982, who, using two-color pyrometer to monitor the temperature history of burning char particles, showed that the temperature of the char was nearly constant during most of the burnout.

What chemical reactions must be considered? As summarized by Field et al., 1967, there are a large number of possible reactions at the char surface and in the boundary layer. On the basis of known chemical kinetics and estimates of the relative concentrations of different chemical species, the significant reactions may be narrowed to the following three:

Thus, we are left with the same basic set of assumptions that most previous researchers have made in order to model char burnout. The char particles are assumed to burn independent of one another in a stagnant continuum of infinite extent. Combustion is assumed to be a pseudo steady-state process which involves no other reactions than 1, 2, and 3.

Controversial Assumptions

In order to complete their models, previous researchers have had to make further assumptions which have not been as easily justified. Typically such assumptions have included the following: reactions 2 and 3 may be ignored, the intrinsic reaction kinetics are fast enough that the combustion rate is limited entirely by bulk mass transfer, and O_2 disassociation in the char boundary layer may be ignored. Each of these assumptions were be reviewed in detail.

Reactions 2 and 3 may be ignored. The extent to which the carbon is oxidized and where the oxidation occurs is directly related to the heat generation rate, and thus, the

particle temperature. Consequently, this issue has received considerable attention over the years.

Several studies (Arthur, 1951; Rossberg, 1956; and Otterbein and Bonnetain, 1968) on the heterogeneous carbon oxidation product have experimentally shown that the CO/CO_2 ratio increases with temperature up to 1700 K. If these results are extrapolated to temperatures in excess of 2000 K, little CO_2 is expected as a heterogeneous combustion product (i.e., reaction 2 negligible). Field et al., 1967, estimated the rate of homogeneous CO oxidation in the char boundary layer and concluded that for a 50 μm char particle, reaction 3 was negligible, but for a 100 μm char particle, reaction 3 would contribute significantly. These early studies were supported by the work of Ayling and Smith, 1972, who successfully modeled their two-color pyrometer data for 10 to 80 μm particles assuming reactions 2 and 3 were negligible.

However, later experiments by Mitchell, 1988, and Waters et al., 1988a, on 100 to 160 μm char particles indicated that reaction 1 alone was not sufficient to account for particle temperatures observed. The results of Mitchell and Waters et al. support the earlier theoretical conclusion of Field et al., 1967, that for larger particles CO oxidation would become important. The most illuminating work on the subject of homogenous CO oxidation is the theoretical work of Haussmann and Kruger, and the experimental work of Tognotti et al. Haussmann and Kruger modeled the gas phase surrounding a burning char particle with a complete set of gas phase kinetics coupled to the char combustion. Tognotti et al. analyzed the combustion products from single particle experiments in an electrodynamic balance. Both researchers concluded that the extent of CO oxidation depends on the particle size, temperature, and gas composition.

Thus, one concludes that reaction 2 is negligible and the importance of reaction 3 will depend on the char size as well as the combustion conditions.

Combustion is limited entirely by bulk mass transfer. The combustion of small particles burning at low temperatures is expected to be significantly influenced by the intrinsic kinetics. Thus, only combustion of large particles at high temperatures is expected to occur at the bulk mass transfer limit.

O_2 disassociation may be ignored. Energy loss is both by conduction and radiation. Energy loss by conduction is directly proportional to the "effective" thermal conductivity of the boundary layer. Hansen, 1959, showed that at 3000 K, O_2 disassociation can increase the thermal conductivity of air (only 20 percent O_2) by a factor of almost 2. For experiments where temperatures of greater than 3000 K are achieved by increasing the O_2 level, sometimes up to 100 percent, O_2 disassociation may significantly increase the thermal conductivity.

3.1.2 This Model

The purpose of this model was to predict the char particle temperature and burning time for the synthetic chars used in the vaporization experiments described in previous quarterly reports. The synthetic chars were size-classified to a mass-mean size of 130 μm , had a very narrow pore size distribution centered about 0.1 μm , had a void fraction of 0.53, and had a specific surface area of 130 m^2/g . The vaporization experiments took place in laminar, entrained-flow reactor with a wall temperature of 1700 K, a gas temperature of 1650 K, a residence time of 0.5s, and an O_2 concentration of 10 to 80 percent. Char temperatures from 2000 to 3000 K were expected. In order to predict burnout times, the model had to be able to handle the initial diameter of 130 μm , as well as all smaller diameters.

Assumptions

The basic assumptions are the same as those of previous researchers which were discussed in the previous section. The controversial assumptions concerning the extent of CO oxidation, the role of the intrinsic kinetics, and the calculation of the gas phase thermal conductivity must each be addressed, as they define this model and distinguish it from all previous models.

Extent of CO oxidation. Given the conditions of the vaporization experiments, the above review indicates that reaction 2 can be neglected but reaction 3 may be significant. Unfortunately, inclusion of gas phase kinetics for homogenous oxidation in the boundary layer complicates this model too severely. Consequently, a lumped approach was taken where reactions 1 and 3 were added (noting that reaction 1 goes to completion and 3 does not) to give the following reaction:

where ψ = moles O_2 consumed/mole C, and $1/2 \leq \psi \leq 1$. This reaction is assumed to occur at the char surface and the enthalpy change of reaction is given by the following equation:

$$\Delta H_{\text{rxn 4}}^\circ = 2(1-\psi) \Delta H_{\text{rxn 1}}^\circ + 2(\psi-1/2) \Delta H_{\text{rxn 2}}^\circ \quad (1)$$

where the enthalpy change for reactions 1 and 2 can be found in the JANAF Thermochemical Tables (Stull and Prophet, 1971). The enthalpy change for reactions 1 and 2 are nearly constant from 1700 to 3200 K and have been fit to the following functions of particle temperature, T_p :

$$\Delta H_{\text{rxn 1}}^\circ = (-8.5\text{J}/(\text{mole}\cdot\text{K})) \times T_p + (-102375\text{J}/\text{mole}) \quad (2)$$

$$\Delta H_{\text{rxn } 2}^{\circ} = (-2.9\text{J}/(\text{mole}\cdot\text{K})) \times T_p + (-391155\text{J}/\text{mole}) \quad (3)$$

The O_2/C ratio, ψ , is a function of char size, char temperature, and gas composition. Determination of ψ for various conditions is of obvious importance and is discussed in detail in one of the following sections.

Role of the intrinsic reaction kinetics. The most appropriate kinetics found for the synthetic chars used in this project were those of Waters et al., 1988b. From measurements between 1300 and 2300 K they report that the combustion of a given char was zero-order in O_2 , had an activation energy of 42 kcal/mole, and a pre-exponential constant of $1.33 \text{ mole}/\text{cm}^2\text{s}$. Using these kinetic constants, intrinsic kinetics were estimated to significantly influence the reaction at particle temperatures less than 2200 K or particle diameters less than $80 \mu\text{m}$. Given that this model was to be used to model chars at temperatures as low as 2000 K and all diameters less than $130 \mu\text{m}$, intrinsic kinetics had to be included in the model.

Calculation of thermal conductivity. Given that the combustion conditions in this work included O_2 concentrations from 10 to 80 percent and char particle temperatures were expected in excess of 3000 K, consideration had to be given to the effect of O_2 disassociation on the thermal conductivity of the gas in the char boundary layer. Details of the thermal conductivity estimations are given in one of the following sections.

Calculation Approach

The assumptions of the previous section define the model. The char particles burn independent of one another in a stagnant gas of infinite extent. Combustion is a steady state process. Carbon monoxide is the sole heterogeneous oxidation product. Homogeneous CO oxidation is coupled with heterogeneous CO formation by means of reaction 4. Intrinsic kinetics must be included in the calculation of the reaction rate and O_2 disassociation must be accounted for in the thermal conductivity of the boundary layer.

Heat Balance. Given that the particle is burning in steady-state, the following energy balance may be written around the particle:

$$Q_{\text{gen}} = Q_{\text{loss}} \quad (4)$$

where: Q_{gen} = rate of energy generation
 Q_{loss} = rate of energy loss

The rate of energy generation is simply the reaction rate multiplied by the enthalpy change of reaction.

$$Q_{\text{gen}} = J_{\text{CO}_x} \Delta H_{\text{rxn}}^{\circ} \quad (5)$$

where: J_{CO_x} = molar flow of CO and CO₂ away from particle

The rate of energy generation may be rewritten in terms of the O₂ flow instead of the CO_x flow. Noting that the direction of flow of O₂ is opposite to that of the carbon oxides,

$$J_{\text{CO}_x} = -(1/\psi) J_{\text{O}_2} \quad (6)$$

where: ψ = moles O₂/mole C

Remembering the basic assumption that the particle exists in a stagnant medium of infinite extent, the rate of energy loss is composed of two parts: conduction and radiation.

$$Q_{\text{loss}} = Q_{\text{cond}} + Q_{\text{rad}} \quad (7)$$

where: Q_{cond} = rate of energy loss via conduction
 Q_{rad} = rate of energy loss via radiation

The rate of energy loss via conduction can be described as the energy flux multiplied by the area.

$$Q_{\text{cond}} = q_{(\text{at } r)} A_{(\text{at } r)} \quad (8)$$

where: r = radius from center of char particle
 q = energy flux
 A = area

The energy flux, q , is given by Fourier's law of conduction,

$$q = -k \nabla T \quad (9)$$

where: k = thermal conductivity

which when applied to our spherically symmetric problem in the absence of convection becomes

$$q = -k \frac{dT}{dr} \quad (10)$$

Combining Eq. (10) and (8) gives the following differential equation.

$$Q_{\text{cond}} = \left[-k \frac{dT}{dr} \right] (4\pi r^2) \quad (11)$$

which may be rearranged and then integrated between the surface of the particle and infinity.

at the char surface: $r = r_p$, $T = \text{particle temperature, } T_p$

at infinity: $r = \infty$, $T = \text{gas temperature, } T_g$

$$Q_{\text{cond}} \int_{r=r_p}^{r=\infty} d(1/r) = 4\pi \int_{T=T_p}^{T=T_g} k dT \quad (12)$$

The thermal conductivity, k , is a function of temperature; however, if k is replaced by the appropriate constant, k_{eff} , Eq. (12) can be integrated to give the following algebraic equation:

$$Q_{\text{cond}} = 4\pi r_p \int_{T=T_g}^{T=T_p} k dT = 4\pi r_p k_{\text{eff}} (T_p - T_g) \quad (13)$$

where: $k_{\text{eff}} = \text{effective thermal conductivity}$

The calculation of k_{eff} is discussed in detail in the following section.

The rate of energy transfer between gray surfaces via radiation may be written as

$$Q_{12} = \sigma F_{12} A_1 (T_1^4 - T_2^4) \quad (14)$$

where: $\sigma = \text{Stefan-Boltzmann constant}$
 $F_{ij} = \text{overall interchange factor}$
 $A_i = \text{external surface area of object } i$
 $T_i = \text{temperature of object } i$

If surface 2 completely surrounds surface 1, the overall interchange factor may be expressed as follows:

$$F_{12} = \frac{1}{(1/\epsilon_1) + (A_1/A_2) [(1/\epsilon_2) - 1]} \quad (15)$$

where: ϵ_i = emissivity of object i

For our system, object 1 would be the char and object 2 would be the furnace wall. Thus, $A_1 \ll A_2$, $F_{12} = \epsilon_1$, and the rate of energy transfer via radiation from the char to the furnace wall can be written as follows:

$$Q_{\text{rad}} = \sigma (4\pi r_p^2) \epsilon_p (T_p^4 - T_w^4) \quad (16)$$

where:
 r_p = radius of char particle
 ϵ_p = emissivity of char particle
 T_p = particle temperature
 T_w = wall temperature

Substituting Eqs. (6), (7), (13), and (16) into Eq. (4), the heat balance becomes:

$$\begin{aligned} J_{\text{CO}_x} \Delta H_{\text{rxn } 4}^\circ &= -(1/\psi) J_{\text{O}_2} \Delta H_{\text{rxn } 4}^\circ \\ &= 4\pi r_p k_{\text{eff}} (T_p - T_g) + \sigma (4\pi r_p^2) \epsilon_p (T_p^4 - T_w^4) \end{aligned} \quad (17)$$

At this point it is obvious that we need either J_{CO_x} or J_{O_2} as a function of T_p .

J_{CO_x} Calculated from Internal Transport and Reaction. This is the classical problem of diffusion and reaction in a porous sphere which can be found in detail in most chemical reaction engineering texts. The rate of carbon oxide flow away from the particle is equal to the product of the maximum intrinsic reaction rate (R_i^{max}), the total surface area of the particle (A_p), and an effectiveness factor (η).

$$J_{\text{CO}_x} = R_i^{\text{max}} A_p \eta = R_i^{\text{max}} (S_p \rho_p V_p) \eta \quad (18)$$

where:
 S_p = specific surface area = $130 \text{ m}^2/\text{g}$
 ρ_p = particle density = 0.94 g/cm^3
 V_p = particle volume = $(4/3)\pi r_p^3$
 r_p = particle radius

The intrinsic rate can be expressed in Arrhenius form as follows:

$$R_i = A_i e^{(-E_a/RT_p)} (cX_{O_2})^n = k_i (cX_{O_2})^n \quad (19)$$

where:
 k_i = preexponential constant
 E_a = activation energy
 T_p = particle temperature
 X_{O_2} = mole fraction O_2
 c = gas concentration
 n = reaction order

The maximum intrinsic reaction rate, $R_i^{\max}$, is simply the intrinsic rate evaluated at the surface concentration, $X_{O_2}^s$.

The most appropriate intrinsic kinetics found for the chars used in this work were those of Waters et al., 1988b. From measurements between 1300 and 2300 K Waters et al. reported that the combustion of a saran char was zero-order in O_2 , had an activation energy of 42 kcal/mole, and preexponential constant of 1.33 mole/cm²s.

The effectiveness factor, η , is a function of the dimensionless Thiele modulus, ϕ , which is a ratio of the rate of reaction to the rate of diffusion.

$$\phi = r_p \left[\frac{\frac{1}{2} k_i S_p \rho_p [cX_{O_2}^s]^{n-1}}{D_{eff}} \right]^{1/2} \quad (20)$$

where:
 D_{eff} = effective diffusivity within the particle
 r_p = particle radius

The Thiele modulus should be corrected for Stefan-flow. For our case this correction takes the form of a slightly altered surface concentration. Assuming that the only product of combustion within the char is CO, the following expression for the corrected surface concentration is easily derived.

$$X_{O_2}^s \text{ (corrected)} = \ln (1 + X_{O_2}^s) \quad (21)$$

The effective diffusivity is generally a combination of bulk diffusivity, which dominates in the large pores, and Knudsen diffusivity, which dominates in the small pores. However, the synthetic chars used in this study had a very narrow pore size distribution

centered about $0.1 \mu\text{m}$. For a pore size of $0.1 \mu\text{m}$ and a temperature between 2000 and 3000 K, the Knudsen diffusivity is always at least an order of magnitude smaller than the bulk diffusivity; therefore, the bulk diffusion may be neglected. Thus, the effective diffusivity in the synthetic chars was simply the Knudsen diffusivity multiplied by the void fraction and divided by the tortuosity.

$$D_{\text{eff}} = (4/3) r_{\text{pore}} \left[\frac{2RT_p}{M_{\text{O}_2} \pi} \right]^{1/2} \left[\frac{\theta_p}{\tau_p} \right] \quad (22)$$

where:
 r_{pore} = pore radius = $0.05 \mu\text{m}$
 θ_p = void fraction = 0.53
 τ_p = tortuosity = 4
 R = ideal gas constant
 M_{O_2} = molecular weight of oxygen

Now we have everything needed to calculate ϕ , but we need the relationship between η and ϕ in order to determine η . The functional form of the relationship between ϕ and η depends on n , the reaction order. However; at values of ϕ greater than 15, all the functional forms for a sphere approach $\eta = 3/\phi$.

Given the physical properties of the char of interest, initial diameter of $130 \mu\text{m}$, kinetics of Waters et al., 1988b, particle temperatures as low as 2000 K, and the mole fraction oxygen at the surface as high as 0.5, ϕ was estimated to be greater than 60 for all conditions at burnouts up to 90 wt%. Thus, the asymptotic relation, $\eta = 3/\phi$, will suffice.

We now have $J_{\text{CO}_x} = f(X_{\text{O}_2}^s, T_p \text{ and } r_p)$; however, we have introduced a new unknown, $X_{\text{O}_2}^s$. We need another equation which we will get from external mass transport.

J_{O_2} Calculated from External Transport. The flow of O_2 to the particle can be written as the molar flux multiplied by the area.

$$J_{\text{O}_2} = j_{\text{O}_2}(\text{at } r) A_{(\text{at } r)} \quad (23)$$

where: J_{O_2} = molar flow of O_2 away from the particle

Remembering the basic assumption that forced convection is negligible, the molar flux of O_2 may be expressed as the sum of the flux due to diffusion and that due to Stefan-flow.

$$j_{O_2} = -cD_{O_2} \left[\frac{dX_{O_2}}{dr} \right] + X_{O_2} \sum_{i=1}^m j_i \quad (24)$$

where: j_i = molar flux of species i
 D_{O_2} = bulk diffusivity of O_2
 c = gas concentration
 X_{O_2} = mole fraction O_2

The sum of the fluxes may be expanded as follows:

$$\sum_{i=1}^m j_i = j_{O_2} + j_{N_2} + j_{CO} + j_{CO_2}$$

$$j_{N_2} = 0$$

$$j_{CO} = \frac{-2(1-\psi)}{\psi} j_{O_2} \quad (25)$$

$$j_{CO_2} = \frac{-2(\psi-1/2)}{\psi} j_{O_2}$$

$$\psi = \text{moles } O_2 / \text{mole } C$$

$$\sum_{i=1}^m j_i = j_{O_2} (1 - (1/\psi)) \quad (26)$$

Substituting Eq. (26) back into Eq. (24), the O_2 flux may be rewritten as

$$j_{O_2} = \frac{-cD_{O_2}}{[1 - X_{O_2} (1 - (1/\psi))]} \left[\frac{dX_{O_2}}{dr} \right] \quad (27)$$

Substituting Eq. (26) back into Eq. (23), the molar flow of O_2 may be written as the following differential equation:

$$J_{O_2} = \frac{-4\pi r^2 cD_{O_2}}{[1 - X_{O_2} (1 - (1/\psi))]} \left[\frac{dX_{O_2}}{dr} \right] \quad (28)$$

Equation (28) may be rearranged and then integrated from the surface of the particle to infinity.

at the char surface: $r = r_p$, $X_{O_2} = X_{O_2}^s$

at infinity: $r = \infty$, $X_{O_2} = X_{O_2}^b$

$$\begin{aligned} -\frac{J_{O_2}}{4\pi} \int_{r=r_p}^{r=\infty} \frac{dr}{cD_{O_2} r^2} &= \int_{X_{O_2}=X_{O_2}^s}^{X_{O_2}=X_{O_2}^b} \frac{dX_{O_2}}{[1 + X_{O_2} ((1/\psi) - 1)]} \\ &= \frac{1}{((1/\psi) - 1)} \ln \left[\frac{1 + X_{O_2}^b ((1/\psi) - 1)}{1 + X_{O_2}^s ((1/\psi) - 1)} \right] \end{aligned} \quad (29)$$

At this point one recognize that cD_{O_2} is a function of temperature which is a function of r . fortunately, cD_{O_2} is a well-behaved function that varies only slightly ($cD_{O_2} = 27E-6$ mole/(cm·s) at $r = \infty$ where the gas temperature = 1650 K and is never expected to be greater than $41E-6$ mole/(cm·s) which is for gas temperature = 3200 K). Therefore, a mean value for cD_{O_2} , taken at $T_m \equiv (T_g + T_p)$, was assumed to sufficiently model the boundary layer.

Thus, the integral on the left side of Eq. (29) may be integrated to give the following equation:

$$J_{O_2} = \frac{4\pi r_p \overline{cD_{O_2}}}{((1/\psi) - 1)} \ln \left[\frac{1 + X_{O_2}^b ((1/\psi) - 1)}{1 + X_{O_2}^s ((1/\psi) - 1)} \right] \quad (30)$$

where: $\overline{cD_{O_2}} = cD_{O_2}$ evaluated at T_m

Equation (30) can be rewritten in terms of the mole fraction O_2 at the char surface.

$$X_{O_2}^s = \frac{\exp \left[\ln \left[1 + X_{O_2}^b ((1/\psi) - 1) \right] + \frac{J_{O_2} ((1/\psi) - 1)}{4\pi r_p \bar{c} D_{O_2}} \right] - 1}{((1/\psi) - 1)} \quad (31)$$

Algorithm. The energy balance produced in Eq. (17) which gives $T_p = f(J_{CO_x}, r_p, T_g, \text{ and } \psi)$. The internal transport and reaction produced Eq. (18) which gives $J_{CO_x} = f(X_{O_2}^s T_p, \text{ and } r_p)$. The external transport produced Eq. (31) which gives $X_{O_2}^s = f(J_{O_2}, T_p, T_g, X_{O_2}^b, \psi, \text{ and } r_p)$. A fourth equation (6) can be written to relate J_{O_2} to J_{CO_x} through the stoichiometry of the oxidation reaction. Thus, there are four equations and eight variables (J_{O_2} , J_{CO_x} , T_p , T_g , r_p , ψ , $X_{O_2}^s$, and $X_{O_2}^b$).

The gas temperature and mole fraction oxygen in the bulk were fixed. The char was assumed to burn in pseudo steady-state; therefore, the particle radius was fixed. The reaction stoichiometry, ψ , was chosen empirically. This leaves 4 unknowns: T_p , J_{O_2} , J_{CO_x} , and $X_{O_2}^s$.

Unfortunately, an explicit solution to the above four equations was not possible. An iterative approach was taken and is illustrated in Figure 3-1. The calculation algorithm began with the input of the bulk oxygen concentration, the particle size, and the O_2/C ratio. The particle temperature and oxygen concentration at the char surface were then assumed. With these inputs and assumptions, along with the kinetics of Waters et al., 1988b, the reaction rate was calculated by means of Eq. (18). The reaction rate was then related to the oxygen flow, J_{O_2} , by means of Eq. (6). This oxygen flow was then used in Eq. (31) to calculate the oxygen concentration at the char surface. The original assumed value for the oxygen concentration at the char surface was then compared to the calculated value. If the values were not close enough, a new value was assumed and the process was repeated. If the values were sufficiently close, then, *for that temperature*, the oxygen concentration at the char surface was correct.

The next step was to determine if the assumed temperature was correct. The energy generation rate was calculated from the previously determined reaction rate using Eq. (5). A second temperature was assumed and the rate of energy loss, based on the second assumed temperature, was calculated from Eq. (7). The second temperature was increased until the heat balance was satisfied and the rate of energy loss was equal to the rate of energy generation. If the temperature which satisfied the heat balance was not sufficiently close to

B-6072

Figure 3-1. Temperature Calculation Algorithm

the original assumption for particle temperature, then a new particle temperature was assumed and the entire process was repeated. If the two temperatures were close enough to satisfy the convergence criteria, then the calculation was complete.

Two of the model inputs have not yet been sufficiently defined: the effective thermal conductivity of the boundary layer and the O_2/C ratio. These inputs are the subjects of the next two sections.

Effective Thermal Conductivity of the Boundary Layer

Equation (13), repeated here, which define the effective thermal conductivity,

$$Q_{\text{cond}} = 4\pi r_p \int_{T=T_g}^{T=T_p} k dT = 4\pi r_p k_{\text{eff}} (T_p - T_g) \quad (13)$$

may be written as

$$k_{\text{eff}} \equiv \frac{\int_{T=T_g}^{T=T_p} k dT}{T_p - T_g} \quad (32)$$

Obviously we need k as a function of T in order to find $k_{\text{eff}} = f(T_p \text{ and } T_g)$. In order to accurately determine $k = f(T)$, we must consider the effects of O_2 disassociation.

In all conduction problems a temperature gradient exists. If the temperature gradient occurs in a gas mixture which is in chemical equilibrium, the equilibrium, and hence the gas composition may change along the temperature gradient. As diffusion and conduction occur along the temperature gradient, some chemical energy, as well as thermal energy, may be transported along the gradient. Thus, the thermal conductivity of a gas mixture will be increased if a temperature sensitive reaction exists in equilibrium along the temperature gradient. The reaction of interest in a mixture of O_2 and N_2 at temperatures between 1650 and 3200 K is O_2 disassociation.

Butler and Brokaw, 1957, report that the thermal conductivity of a reacting gas mixture in chemical equilibrium is the sum of the hypothetical thermal conductivity of the gas mixture without the reaction, k_n , and the thermal conductivity due to the reaction, k_r .

$$k = k_n + k_r \quad (33)$$

The thermal conductivity of a nonreactive gas mixture is not usually a linear function of the mole fraction. If the molecules are polar, the thermal conductivity is generally larger than would be predicted from a mole fraction average. If the molecules have large differences in molecular weight, the thermal conductivity is generally less than would be predicted from a mole fraction average. The gases of interest in this study are mixtures of O_2 and N_2 which are both nonpolar and have similar molecular weights. Thus, a mole fraction average should closely approximate the hypothetical thermal conductivity of the gas without reaction.

$$k_n = X_{O_2}^b k_{O_2} + X_{N_2}^b k_{N_2} \quad (34)$$

where: X_i^b = mole fraction species i without disassociation
 k_i = thermal conductivity of pure i without disassociation

In order to calculate k_n , pure component thermal conductivities for molecular nitrogen and molecular oxygen were required. Nitrogen does not disassociate significantly at 1 atm of pressure until the temperature exceeds 4000 K. Thus, the pure component thermal conductivity of N_2 can be measured directly and was taken from the National Bureau of Standards publication NSRDS-NBS 8 by Powell et al., 1966. The thermal conductivity ranged from $0.95E-3$ J/cms K at 1700 K to $1.74E-3$ J/cms K at 3200 K.

Oxygen begins to disassociate significantly at temperatures as low as 2200 K at 1 atm of pressure. Thus, the thermal conductivity of molecular O_2 without dissociation is hypothetical at temperatures greater than 2200 K and, thus, cannot be measured. The hypothetical thermal conductivity of molecular oxygen was calculated by the method of Chung et al., 1984. The method of Chung et al., requires the gas molecular weight, acentric factor, viscosity, and heat capacity. The heat capacity of molecular oxygen was taken from the JANAF Thermochemical Tables (Stull and Prophet, 1971) and the viscosity of molecular oxygen was calculated using the Chapman-Enskog equation with the Leonard-Jones intermolecular force law. The acentric factor and the Leonard-Jones parameters were taken from Reid et al., 1987. The thermal conductivity of molecular O_2 was calculated to be $1.10E-3$ J/cms K at 1700 K and $1.79E-3$ J/cms K at 3200 K, very close to the values for molecular N_2 .

The reactive thermal conductivity was given by Butler and Brokaw, 1957, as the following:

$$k_r = \frac{R \left(T \frac{d \ln K}{dT} \right)^2}{\sum_{j=1}^{\mu-1} \sum_{m=j+1}^{\mu} \left[\frac{RT}{D_{mj}P} \right] \left[\frac{(a_j X_m - a_m X_j)^2}{X_m X_j} \right]} \quad (35)$$

where:

- μ = total number of species = 3(O₂, N₂, O)
- D_{mj} = diffusivity of species m in species j
- R = ideal gas constant
- T = temperature
- K = equilibrium constant for reaction 5
- a_j = stoichiometric coefficient for species i in reaction 5
($a_{N_2} = 0$, $a_{O_2} = -1$, $a_O = 2$)
- X_i = mole fraction species i

When applied to reaction 5, the denominator of Eq. (35) expands to the following expression:

$$\left[\frac{1}{D_{O-O_2}} \right] \left[\frac{(X_O + 2X_{O_2})^2}{X_O X_{O_2}} \right] + \left[\frac{1}{D_{N_2-O_2}} \right] \left[\frac{X_{N_2}}{X_{O_2}} \right] + \left[\frac{1}{D_{N_2-O}} \right] \left[\frac{4X_{N_2}}{X_O} \right]$$

and numerator of Eq. (35) may be rewritten as:

$$\frac{(\Delta H_{rxn \ 5}^\circ)^2}{RT^2}$$

The mole fractions of each species, the diffusivities, and the change in enthalpy of reaction 5 are all functions of temperature. The mole fractions of each species are also a function of the initial gas composition before disassociation. The change in enthalpy of reaction 5 was calculated from data taken from the JANAF Thermochemical Tables (Stull and Prophet, 1971). The diffusivities were calculated using the Chapman-Enskog equation with the Leonard-Jones intermolecular force law.

In order to determine the mole fractions of each species, one can write the following six equations:

$$X_O \equiv n_O/n_t \quad (36)$$

$$X_{O_2} \equiv n_{O_2}/n_t \quad (37)$$

$$X_{N_2} \equiv n_{N_2}/n_t \quad (38)$$

$$n_t \equiv n_O + n_{O_2} + n_{N_2} \quad (39)$$

$$N_{O_2}^{\circ} = n_{O_2} + 1/2 n_O \quad (40)$$

$$K = X_O^2/X_{O_2} \quad (41)$$

where: n_i = moles of species i
 n_t = total moles
 n_i° = initial moles of species i without disassociation
 X_i = mole fraction species i
 K = equilibrium constant for reaction 5

Equations (36) through (39) are simply definitions, Eq. (40) represents an atom conservation balance for oxygen, and Eq. (41) represents chemical equilibrium. These equations may be solved to give the mole fraction of each species as a function of the equilibrium constant and the mole fraction O_2 before disassociation.

$$X_O = \left[(1/16)K^2 + (1/8)K^2 X_{O_2}^b + (1/16)K^2 X_{O_2}^{b^2} + K X_{O_2}^b \right]^{1/2} - K \left[1 + X_{O_2}^b \right] / 4 \quad (42)$$

$$X_{O_2} = \frac{X_O^2}{K} \quad (43)$$

$$X_{N_2} = 1 - X_O - X_{O_2} \quad (44)$$

The equilibrium constant was determined as a function of temperature from data taken from the JANAF Thermochemical Tables.

We now have all the necessary equations to estimate the thermal conductivity from Eq. (33) as a function of both temperature and initial mole fraction oxygen. The thermal conductivity ranges from $0.96E-3$ J/(cm·s·K) for 5 percent O_2 in N_2 at 1700 K to $9.39E-3$ J/(cm·s·K) for 100 percent O_2 at 3200 K.

A comparison of the above thermal conductivities calculated with accounting for O₂ disassociation (k) to the thermal conductivity calculated without accounting for O₂ disassociation (k_n) is shown in Figure 3-2 which is a plot of k/k_n versus temperature. Figure 3-2 illustrates the lack of importance of O₂ dissociation on char particles burning in 10 percent O₂, which are not expected to achieve temperatures greater than 2000 K. However, for chars burning in 100 percent O₂, particle temperatures are expected to exceed 3000 K, in which case O₂ disassociation will clearly have a significant influence on the thermal conductivity of the boundary layer.

This brings us back to the purpose of this section which was to determine the effective thermal conductivity of the boundary layer as described in Eq. (32).

$$k_{\text{eff}} = \frac{\int_{T_g}^{T_p} k dT}{T_p - T_g} \quad (32)$$

Equation (32) was numerically integrated using the above calculated values for $k = f(X_{\text{O}_2}^b, T)$ to give $k_{\text{eff}} = f(X_{\text{O}_2}^b, T_g, T_p)$. The bulk gas temperature, T_g , was 1650 K in all experiments. For purposes of modeling, k_{eff} , was fit to a fifth order polynomial function of T_p for each value of $X_{\text{O}_2}^b$.

Choice of O₂/C Ratio

As discussed in the review of previous work, heterogeneous CO₂ formation is negligible under the conditions of interest; however, CO oxidation in the boundary layer may be significant depending on the particle size and combustion conditions. In one of the previous sections a lumped approach was outlined to handle the heterogeneous CO formation and homogeneous CO oxidation as one reaction occurring at the char surface.

The model was developed with, ψ , the O₂/C ratio in the lumped reaction as a variable. The O₂/C ratio is the last remaining input required for this model and must be determined empirically. Thus, a further review of the literature is required.

Haussmann and Kruger modeled the gas phase surrounding a burning char particle with a complete set of gas phase kinetics coupled to the char combustion. They reported the dependence of particle temperature on radius, oxygen concentration, water concentration, and gas temperature. Unfortunately, their work was strictly theoretical, they reported only how

B-6071

Figure 3-2. Effect of Oxygen Disassociation on Thermal Conductivity

the above variables influenced the particle temperature, with no mention of the extent of CO oxidation, and they only considered oxygen concentrations up to 25 percent.

Waters et al., 1988a, performed experimental work on spherical carbon particles between 100 and 160 μm . The particles were burned in 12 to 36 percent O_2 and 14 to 20 percent H_2O , at a gas temperature of 1775 K. The particles achieved temperatures of 1400 to 2200 K. In order to account for the observed particle temperatures, homogeneous CO oxidation was assumed to occur in the boundary layer. In order to model the CO oxidation in the boundary layer, Waters et al. fit their results using an adjustable parameter which represented the fraction of the energy released from a hypothetical complete CO oxidation. The best fit of this parameter to all their experimental data was 0.35. This is virtually the same approach as taken in the model developed herein. Their value of 0.35 corresponds to $\psi = 0.5 + 1/2(0.35) = 0.675$. Unfortunately, they fit all their data for all their conditions to a single parameter, neglecting the expected dependence of the parameter on gas concentration and particle temperature. Furthermore, their experiments were run in gases with extremely high water contents, which, given the importance of H_2O catalysis in homogeneous CO oxidation, makes their results completely inapplicable to the experiments of this thesis, which were run dry.

Tognotti et al, 1990, analyzed the combustion products from single particle experiments in an electrodynamic balance. Tognotti et al. directly measured the CO_2/CO ratio after complete combustion of 180 to 240 μm spherical particles. Tognotti et al. were able to experimentally verify the importance of the water content and particle temperature on the CO_2/CO ratio. The CO_2/CO ratio was at a minimum of approximately 0.1 at a particle temperature of 1500 K. The CO_2/CO ratio increased at lower temperatures due to heterogeneous CO_2 formation and at higher temperatures due to homogeneous CO oxidation. In the environment of 20 percent O_2 , no added water, and a particle temperature of 2000 K, 15 percent of the CO was oxidized ($\psi = 0.5 + 1/2 \times 0.15 = 0.575$). In the environment of 100 percent O_2 and no added water, the Tognotti et al. results only cover particle temperatures from 2000 to 2500 K. If the results are extrapolated to 3000 K, approximately 70 percent of the CO would be expected to oxidize ($\psi = 0.5 + 1/2 \times 0.7 = 0.85$). These conditions of no water, 2000 K with 20 percent O_2 , and 3000 K with 100 percent O_2 are approximately what was expected in the experiments of this study.

Unfortunately, three problems develop when trying to incorporate the Tognotti et al. data into our current model. First, the particle sizes were different. The relevant experiments of this project were performed with 130 μm chars, while the Tognotti et al. data was collected using 180 to 240 μm chars. The size of the char is directly proportional to the size of the boundary layer. Consequently, the extent of CO oxidation in the boundary layer is a strong function of particle size (Field et al., 1967). Second, the data exist only at 20 and 100 percent O_2 . Third, the data are the integrated sum of the CO and CO_2 produced over the entire burnout, but the model of this study is for a single char radius burning under pseudo steady-state conditions.

The data of Tognotti et al. were the most applicable; therefore, each of the above problems was addressed as well as possible.

Effect of char particle size. In order to correct the Tognotti et al. data for the smaller particles used in this thesis, the relation between the O_2/C ratio (ψ) and the char radius (r_p) was required. Haussmann and Kruger reported the increase in particle temperature due to homogeneous CO oxidation (ΔT_p) was approximately proportional to r_p^2 . In order to use this relation, the relationships between ΔT_p and ψ was required. The model developed in the previous sections was used to determine the relation between ΔT_p and ψ . Figure 3-3 shows how the predicted particle temperature increased as ψ as increased from the minimum value of 0.5 ($\psi = 0.5$ corresponds to no CO oxidation). Figure 3-3 shows the model results for a 130 μm char particle at both 20 and 100 percent O_2 . The increase in particle temperature, ΔT_p , was approximately proportional to $(\psi - 0.5)^{0.7}$. Thus, if we combine this result with the relation between ΔT_p and ψ from Haussmann and Kruger, the following equation may be written:

$$(\psi - 0.5)^{0.7} \propto r_p^2 \quad (45)$$

Using Eq. (45), the data of Tognotti et al. were corrected to particles of 130 μm to give $\psi = 0.52$ at 20 percent O_2 and 2000 K, and $\psi = 0.59$ at 100 percent O_2 and 3000 K.

Data exist only at 20 and 100 percent O_2 . Lacking a better method of extrapolation, the data at 20 and 100 percent O_2 were linearly extrapolated to other O_2 concentrations. Thus, values of ψ of 0.507, 0.511, 0.520, 0.529, 0.546, 0.573, and 0.590 were used for O_2 concentrations of 5, 10, 20, 30, 50, 80, and 100 percent O_2 , respectively.

Data are from complete burnout. The model of this thesis is for a char of constant size burning in pseudo steady-state; therefore, data for CO/CO₂ ratio as a function of burnout would be desirable. Unfortunately, the Tognotti et al. data are the integrated sum of the CO and CO₂ produced over the entire burnout and differentiation of that data seems impossible. However, since the model was to be used at the initial radius and then incrementally smaller radii to simulate burnout (see Tables 3-1 and 3-2), the values of ψ determined from the Tognotti data were simply assumed to remain constant all through burnout.

Clearly, the choice of ψ has been difficult and a sensitivity analysis is in order. Figure 3-3 is a sensitivity analysis. At 20 percent O_2 a value of ψ of 0.52 was chosen. This corresponds to 4 percent of the CO oxidized to CO₂ in the boundary layer. The error in the predicted temperature if the actual percentage of CO oxidized is 1/2 or twice the estimated 4 percent is +15 or -50 K, respectively. At 80 percent O_2 a value of ψ of 0.573 was chosen. This corresponds to approximately 15 percent of the CO oxidized to CO₂ in the boundary layer. The error in the predicted temperature if the actual percentage of CO oxidized is 1/2 or twice the estimated 15 percent is +60 or -115 K, respectively.

B-6070

Figure 3-3. Effect of the O_2/C Ratio on the Predicted Particle Temperature

Model Results

Given the calculations for the effective thermal conductivity and the estimates for the O_2/C ratios in the two previous sections, the model was complete.

In order to simulate char burnout, the model was used to calculate the char temperature and burning rate for the initial diameter of $130\ \mu\text{m}$ and 12 subsequent diameters. The results for two combustion conditions, 10 and 80 percent O_2 , are shown in Tables 3-1 and 3-2. As seen in Tables 3-1 and 3-2, the particle temperature falls off dramatically in the later stages of burnout. This temperature decline in the later stages of burnout happens because the particle shrinks and approaches the kinetic regime. As the particle nears the kinetic regime, energy generation is proportional to between r_p^2 and r_p^3 , depending on the effectiveness factor. The energy loss is independent of combustion regime and is proportional to between r_p^2 and r_p , depending on the relative importance of radiation and conduction. Thus, the heat generation rate falls off more rapidly than the heat loss rate as the particle shrinks toward the kinetic regime; consequently, the particle cools.

The burning rate was used to calculate the incremental burning time for each increment in particle size. The incremental burn times were then summed to give the total burnout time.

Three differently weighted average temperatures, the maximum temperature, and the total burnout time are summarized in Table 3 for a range of O_2 concentrations. The first average reported was time-weighted over complete burnout. This average is very sensitive to the long, and relatively cool, final stages of burnout. The sensitivity of the first average to the final stages of burnout is emphasized by showing that a second average, which was weighted over the first 99.95 wt% of burnout, was significantly different than the first average.

A third average was required for the interpretation of the vaporization data presented in the last quarterly report. Given that the vaporization which occurs during any incremental stage of burnout is proportional to both the burn time for that increment and the volume of total char remaining as that increment burns, a time and volume weighted average was desired. However, vaporization is also an exponential function of particle temperature and an unknown function of the reducing atmosphere within the particle. Thus, the last stages of burnout, which have low temperatures and high effectiveness factors, are not expected to contribute significantly to vaporization. For the vaporization work discussed in the following chapter, a time and volume weighted average temperature for the first 90 wt% of burnout is also reported in Table 3-3. This average is much greater than the time only weighted averages and only slightly less than the maximum temperature.

Table 3-1. Model Results as a Function of Diameter for
10 Percent Oxygen

10% O₂, O₂/C ratio = 0.511

Particle Diameter (μm)	Particle Temperature (K)	Effectiveness Factor	Reaction Rate (gmolC/s)	Mass Fraction Burned	Incremental Burn Time (s)
130	1915	0.0104	2.79E-7	0	0
120	1910	0.0120	2.44E-7	0.2135	0.074
110	1900	0.0139	2.09E-7	0.3942	0.072
100	1890	0.0165	1.76E-7	0.5448	0.070
90	1880	0.0200	1.44E-7	0.6682	0.069
80	1865	0.0244	1.15E-7	0.7670	0.069
70	1845	0.0310	8.68E-8	0.8439	0.069
60	1820	0.0418	6.12E-8	0.9017	0.070
50	1795	0.0561	4.13E-8	0.9431	0.073
40	1765	0.0798	2.43E-8	0.9709	0.076
30	1735	0.1218	1.26E-8	0.9877	0.082
20	1705	0.2063	5.18E-9	0.9964	0.088
10	1680	0.4685	1.20E-9	0.9995	0.090
0	--	--	--	1.0	0.069

Total burn time = 0.971

Table 3-2. Model Results as a Function of Diameter for
80 Percent Oxygen

80% O₂, O₂/C ratio = 0.573

Particle Diameter (μm)	Particle Temperature (K)	Effectiveness Factor	Reaction Rate (gmolC/s)	Mass Fraction Burned	Incremental Burn Time (s)
130	3020	0.0016	2.66E-6	0	0
120	3030	0.0018	2.42E-6	0.2135	0.008
110	3040	0.0021	2.18E-6	0.3942	0.007
100	3045	0.0024	1.94E-6	0.5448	0.007
90	3055	0.0029	1.70E-6	0.6682	0.006
80	3050	0.0035	1.45E-6	0.7670	0.006
70	3040	0.0044	1.20E-6	0.8439	0.005
60	3020	0.0059	9.46E-7	0.9017	0.005
50	2970	0.0084	6.92E-7	0.9431	0.005
40	2870	0.0136	4.44E-7	0.9709	0.004
30	2655	0.0284	2.16E-7	0.9877	0.005
20	1925	0.2504	2.64E-8	0.9964	0.006
10	1740	0.9600	3.78E-9	0.9995	0.019
0	--	--	--	1.0	0.022

Total burn time = 0.104

Table 3-3. Summary of Model Results

Mole Fraction Oxygen	O ₂ :C Ratio	Average ⁽¹⁾ Particle Temperature (K)	Average ⁽²⁾ Particle Temperature (K)	Average ⁽³⁾ Particle Temperature (K)	Maximum Particle Temperature (K)	Total Burnout Time (s)
0.05	0.507	1750	1755	1800	1805	1.717
0.10	0.511	1810	1820	1895	1915	0.971
0.20	0.520	1930	1955	2135	2160	0.497
0.30	0.529	2055	2105	2395	2410	0.313
0.35	0.533	2110	2170	2505	2515	0.263
0.50	0.546	2265	2370	2750	2770	0.173
0.65	0.559	2385	2540	2915	2930	0.129
0.80	0.573	2480	2675	3035	3055	0.104
1.00	0.590	2600	2845	3150	3165	0.082

(1) time-weighted average over complete burnout

(2) time-weighted average over 99.95 mass% burnout

(3) time-and-volume-weighted average over 90 mass% burnout

3.1.3 Comparison of Model Results to Data from Timothy et al., 1982

In order to check the model results, particularly the effect of the corrected thermal conductivity, a comparison to data was sought. The combustion temperature data of Timothy et al. (1982) was the most appropriate for comparison because it was generated under nearly the same combustion conditions that the model was developed to cover: O_2 concentrations up to 100 percent and gas temperatures of approximately 1650 K. In addition, the data of Timothy et al. was collected using the same size chars. In fact, the only significant difference was that the Timothy et al. data was collected from the combustion of coals, not synthetic chars.

Timothy et al. measured the char combustion temperatures using a two-color pyrometer with a laminar, entrained-flow reactor. The two-color pyrometer was set up to view the particles through the feeder probe. The two-color pyrometer was set up to view the particles through the feeder probe. The particles remained in view of the pyrometer all through burnout; thus, temperature data could be collected for the entire burnout.

Figure 3-4 shows the data collected by Timothy et al. (1982) for 2 different coals: Montana lignite and Illinois #6 bituminous coal. The temperature shown is a time-weighted average over complete burnout. Also shown is the Timothy et al. model assuming bulk gas diffusion limited combustion based on initial diameter with no accounting for O_2 disassociation. The model over-predicted the data at O_2 concentration greater than 50 percent because O_2 disassociation was not included, and under-predicted the data at O_2 concentrations less than 50 percent because the assumption of strict bulk mass transfer limited combustion breaks down and reaction kinetics become important. The difference between the Montana lignite and Illinois #6 bituminous coal was never completely explained, especially at the higher O_2 concentrations where combustion was expected to be limited by bulk gas diffusion only.

The key to explaining the Timothy et al. data is to note how the temperatures were averaged. As seen in the results herein (Tables 3-1 and 3-2), the particle temperature falls off dramatically in the later stages of burnout. This temperature decline in the later stages of burnout happens because the particle shrinks and approaches the kinetic regime. The importance of this temperature decline depends on how the temperature is averaged.

With this in mind, the Timothy et al. model and data should be reconsidered. The Timothy et al. model is clearly a maximum temperature, not a time averaged temperature, because it is based on the initial diameter only. Conversely, the temperature reported for the coals is a time averaged temperature. However, the coals burn out differently. The Illinois #6 bituminous coal particles swell, form a cenosphere, and burn out as a shell. If an Illinois #6 bituminous coal particle had a swelling ratio of 1:15 and a mass loss of 35 wt% on devolatilization, it would burn out as a shell from 150 to 125 μm , all of which would occur at approximately the maximum temperature. Thus, the time-averaged temperature for the Illinois #6 bituminous coal would be very close to the maximum temperature. The

B-6069

Figure 3-4. Temperature Versus Oxygen Concentration, Comparison to Timothy et al. (1982)

Montana ignite, on the other hand, burns as a shrinking core; therefore, its time-weighted average temperature would be substantially less than its maximum temperature.

A model based on the maximum temperature was expected to fit the Illinois #6 bituminous coal temperatures and a model based on the time-averaged temperature was expected to fit the Montana lignite temperatures. Figure 4 shows that the maximum temperature generated from our current model does not fit the data for the Illinois #6 bituminous coal quite well, especially at the higher O₂ concentrations. At the low O₂ concentrations internal transport and reaction become important. This model uses the slower kinetics for synthetic chars and an effective diffusivity based on a strictly microporous char. Thus, at lower O₂ concentrations this model is expected to under-predict coal temperatures, and indeed it does.

Figure 3-4 shows that the time-averaged temperatures generated from the model for complete burnout and for 99.95 wt% of burnout bracket the temperature data for Montana lignite at the highest O₂ concentrations. The actual extent of burnout over which the Montana lignite temperature data was averaged is unknown and may have depended on the signal/noise ratio in the pyrometry signal. The two-color pyrometry signal falls off as r_p^2 . If the noise in the pyrometry signal was 10 percent of the temperature signal, the temperature signal would have been indistinguishable from the noise at 97 wt% burnout (r_p reduced to 32 percent of original r_p). Given the unknown extent of burnout over which the temperature was averaged, and the expected under-prediction of temperature at the lower O₂ concentrations, the model fits the Montana lignite data quite well also.

3.1.4 References for Section 3.1

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3.2 Simulation of Residual Ash Formation with a Continuum Model

3.2.1 Model Assumptions

A Monte Carlo model was developed in a continuum space in order to simulate the growth of flyash particles on a char surface during the char burnout. The model follows the combustion history of a single char particle. Following assumptions were made for the model:

1. *No mineral matter vaporizes during the char combustion:* The amount of mineral matter vaporized during char combustion is negligible, and therefore does not affect the residual ash particle size distribution. Quann et al.[12] investigated ash vaporization under simulated pulverized coal combustion conditions. He found that the amount and composition of the mineral matter that vaporized was strongly dependent on particle temperature and coal type, but did not exceed more than 5 wt% of the total mineral matter.
2. *Fragmentation of mineral matter does not affect the residual ash particle size distribution over the course of the char combustion:* While some mineral matter (e.g., pyrite, and illite) fragments during the combustion, most silicates do not. It is these minerals which constitute the bulk of the mineral matter in coal. Pyrite in coal is prevalent but will only fragment under certain conditions. It is usually the fragmentation of extraneous mineral matter, not inclusions, that influences the final ash particle size distribution. This is because when an inclusion is fragmented into pieces, fragments of the inclusion are buried in (or bound by) the char matrix still held together by the surrounding char matrix until they are exposed to the surface. By the time these fragments of the

mineral inclusion get exposed to the surface, they usually reach a temperature which is high enough to have fragmented inclusions molten. Molten fragments of an inclusion coalesce to form one molten particle. Since the main concern of the model is the formation of residual flyash from inclusions, and not from the extraneous mineral matter, the fragmentation of included mineral matter does not affect our final ash size distribution. In order to get the complete distribution, though, it is necessary to get the information on the behavior of the extraneous mineral matter.

3. *Surface ash particles remain attached to the surface of the char and recedes along with the receding char surface during the char combustion, and are not separated from the char surface by shedding induced by char rotation:* As coal particles begin to devolatilize, gaseous jets of volatiles effusing from the particle give rise to high frequency char particle rotation [8]. The surface tension causes ash particles to adhere to the surface of the burning char. Helble *et al.*[6] showed that the ratio of the sum of the centrifugal and gravitational forces to the adhesion force is less than unity and concluded that at practical combustion conditions the surface tension is high enough to overcome centrifugal force induced by the high frequency rotation of the char.
4. *No ash cenospheres or plerospheres are formed.* Ash cenospheres and plerospheres have been observed by many researchers [13, 3, 16]. Sarofim *et al.* have carried out laboratory scale experiments with a highly swelling Pittsburgh seam bituminous coal and a slightly swelling Montana lignite. They reported the mass fraction of cenospheres by measuring the amount of ash with a specific gravity less than unity. The amount of ash cenospheres produced peaked at furnace temperature of 1500K and was no more than 5 wt% of total ash. At furnace temperature of 1750K, the amount dropped to 3 wt%. The amount of ash plerosphere is also expected to be about the same. Ne-

glecting this insignificant amount of ash cenospheres and plerospheres is not expected to change the overall trend of the ash mass distributions.

5. *Upon contact, two surface ash particles coalesce instantaneously to form one ash particle with the mass of the two particles:* The time required for the formation of an effective particle-to-particle bonding by viscous flow as a result of surface tension can be calculated by the Frenkel equation:

$$x^2 = \frac{3r\gamma t}{2\mu} \quad (1)$$

or,

$$\frac{x}{r} = 1.225 \sqrt{\left(\frac{\gamma}{\mu r}\right)t} \quad (2)$$

where x is the radius of the interface (or the neck) assumed to be circular; t , time; γ , the surface tension; and r , the radius of the spherical particles. The coalescence time of two molten surface ash of radius $5 \mu\text{m}$ can be estimated using equation (2) for an ash surface tension and viscosity of 0.32 N/m and $10^3 \text{ N} \cdot \text{s/m}^2$, respectively. The ratio, x/r , which represents the degree of sintering is taken to be 0.3 for the calculation [13]. The calculation thus made shows that the required coalescence time is only a fraction of a millisecond (0.9 ms). This is negligible compared with the total char burnout time of tens of milliseconds (e.g., 90 ms for Montana lignite 90/106 μm at 1350 K, 20% O_2 [6]).

7. *Pores considered in the model are those macropores resulting in the effectiveness factor greater than 0.9:* At the practical combustion temperature, pores through which full access of O_2 is allowed are those greater than $0.1\ \mu m$. The pores of this size range will mainly affect the change of char morphology as the reaction proceeds.
8. *During the recession, a surface ash particle gets separated when it encounters a pore:* Experimental observation shows that macropores play a vital role on residual ash formation [6]. Non-macroporous char generates one ash per char whereas macroporous char generates many ash particles per char. In our previous on-lattice model (char fragmentation model), this finding is implemented by having the macropores induce the char fragmentation, hence the suppression of ash growth. But in this model, this finding is interpreted otherwise. Oxidation reaction takes place inside macropores being considered in the model. This internal burning undercuts the neck region formed by the char surface and internal surface of a pore, thereby effecting the separation of the surface ash particle from the char.

3.2.2 Model Formulation

Construction of a Char Particle

In the continuum model, a char particle with pores and mineral inclusions is represented as a continuous phase with a collection of non-overlapping spherical, discrete phases distributed randomly. The continuous phase is the carbonaceous material and the discrete phases are pores and mineral inclusions. Their positions and sizes are determined by a random number generator.

Two different char configurations are taken into consideration in the present study in order to study the effect of the finite size of the char on the ash growth

behavior. It is pointed out that due to the increasing curvature of the char particle perimeter, the average surface ash size does not relax to a steady state size, instead increases more rapidly as the reaction draws near to the end [10, 7]. An inflection point, therefore, was predicted to be shown when the average surface ash size is plotted against the char particle radius or fractional conversion [10].

The first configuration constructed is a planar configuration. While most of the coals show finite size effect, swelling coals which form cenospheres are not expected to show any significant finite size effect. These cenosphere forming swelling coals are easily modeled as a char with a planar configuration. In this configuration, a char is considered as a semi-infinite slab of finite thickness and cross section with a periodic boundary condition at the transverse boundaries (i.e., left and front ends of the char are thought to be connected to the right and rear ends, respectively). Pores and inclusions are distributed in the char. The locations are expressed in the (x, y, z) coordinate system. Each component of the coordinate is generated by multiplying a random number between 0 and 1 by the dimension of the direction of interest. The sizes of each of the pores and inclusions, r_p and r_m , are selected to satisfy the desired size distributions. Each time a candidate of a location is generated, an overlap test of the candidate with each of the existing dispersed phase is performed by comparing the distance between centers of the candidate and the existing phase with the sum of their radii. This random generation of a location is repeated until a non-overlapping one is generated. The distribution scheme is iterated until the desired porosity and mineral content is achieved.

The second configuration constructed is a spherical configuration. A char particle is considered in this configuration as a sphere of a given radius, R_c , with pores and inclusions of given sizes dispersed randomly. The char realization scheme is the same as that for planar configuration. The spherical coordinate system of (ρ, θ, ϕ) is used for the locations of each of the pores and inclusions.

Realization of Char Reaction

The reaction of the char is realized as the recession of the char surface in the direction normal to it. The reaction front is defined by the char surface and the internal surface of pores exposed to the environment. The distance the char surface recedes is not uniform, and is dependent upon the location of a dispersed phase. At a certain time step, a dispersed phase nearest to the char surface, whether it be a pore or an inclusion, is located first. The current char surface is then brought down to the location of the phase. The inclusion(s) between the new and old char surface is (are) also brought onto the surface. For the simplicity of the model, the size of the pores exposed to the char surface is assumed to remain the same. The only role of the pores in the model is that they induce the separation of surface ash particles from the body of the char. The simplification of neglecting the pore broadening, therefore, results in an underestimation of the ash separation events. This simplification, however, is not expected to cause any significant difference in the evolution of surface ash.

Surface Ash Growth

As the char surface recedes, the surface ash particles also recede adhered to the surface. At the same time, the receding char surface exposes mineral inclusions buried in the char. As a result, the surface of the char becomes more and more crowded with ash particles. Some of the surface ash particles are close enough to touch each other. Upon contact, these particles coalesce to form one larger surface ash particle. It is a consequence of this touching coalescence that these surface ash particles grow in size. The surface ash keeps growing as the char surface recedes until it encounters an internal pore and gets separated from the body of the char. For touching coalescence, a check for overlap between surface ash particles is performed every time the reaction front recedes. For the separation of the ash particles, a check

for overlap of ash particles with pores is carried out. Those particles overlapping with pores are separated from the carbon and stored in the separated ash bins.

Data Reduction

The separated ash particles are stored in bins of sizes that increases geometrically. The reported size, s of ash particles for the study is by the mass. Setting the minimal size of inclusion equal to 1, the bins set out for the output presentation are for mass of 1, 2 to 3, 4 to 7, 8 to 15, 16 to 31, etc. The representative size of each bin used for the plotting is the geometric mean of the two boundary masses. For example, the representative size for the sixth bin (32 to 63) is 45. This is, of course, for the case in which the size of initial mineral inclusions are integral. The number of flyash particles in bin size s is N_s . In order for the comparison between runs at different char dimensions, the number distribution is normalized by the volume of the initial char, i.e.,

$$n_s = \left[\frac{N_s}{V_{char}} \right] \quad (3)$$

where N_s and V_{char} are the absolute number of flyash particles of size s , and the volume of the initial char, respectively. The *reduced* number n_s is char size-independent, and is used for our study. This is sometimes called the *number density* in our work.

3.2.3. Parameter for Ash Growth

As was mentioned earlier, the ash growth process is a competition between the separation of surface ash from the parent char particle, and the coalescence of surface ash particles along with the addition of mineral inclusions to the existing surface ash particles. The former suppresses the growth of average surface ash size whereas the latter enhances it. The competition can be parametrized by comparing two length scales that can represent these two opposing processes.

Consider a partially reacted char particle in Figure 3-5 in which pores and mineral inclusions are embedded. Now we follow the history a surface ash particle goes through until it encounters and gets separated. Suppose a surface ash particle has already grown to a certain size. This partially grown ash particle travels along with the receding char surface as the char reaction continues until it encounters a mineral inclusion underneath it. The surface ash grows as the underneath mineral inclusion is added to it. The surface ash particle keeps moving down with the char surface sweeping a volume of the char and scavenging mineral inclusions in the volume until it finally comes to sit right on top of the embedded pore. It is at this instant that the surface ash particle gets separated from the parent char and convects away.

In this scenario, we have two different length scales which are related to the ash growth. One is the coalescence distance, L_c , which is the mean distance a surface ash particle travels until it encounters a mineral inclusion and coalesces with it. The other is the separation distance, L_s , which is the mean distance a surface ash particle travels until it gets separated from the char. As L_c increases, the probability of surface ash growth. As L_s increases, on the other hand, so does the probability of a surface ash particle to grow further. When statistically meaningful expressions for these length scales are obtained, the ratio of these two length scales, $\Lambda = L_s/L_c$ can be a useful parameter to describe the surface ash growth, which is the result of the competition between the fragmentation and coalescence. This ratio is expressed in terms of the mean pore diameter, r_p , mean inclusion diameter, r_m , pore volume fraction, ϕ , and the mineral volume fraction, θ .

We now derive the two length scales for both the planar and the spherical char configurations. The parameters obtained from these two relevant length scales can be applied to actual analysis of the ash formation behavior when a careful choice of the input is taken. The planar configuration analysis can be adopted for swelling coals which, after devolatilization, form thin-shelled cenospheres. For coals maintaining its original, roughly spherical shape, the spherical configuration analysis can

B-6068

Figure 3-5. Illustration of the formation of a flyash particle. A surface ash particle coalesces (or scavenges) a mineral inclusion underneath, and grows larger until it encounters a pore and gets separated when it encounters a pore. Two major events (coalescence and separation) are shown in the figure. These events can be quantitatively expressed by deriving statistically meaningful length scales. Open circles and closed circles represent pores and mineral inclusions, respectively. Surface ash particle is also shown as closed circle.

be adopted.

Ash Growth Number in Planar Configuration

Separation Length Scale, L_s

The separation length scale in a given system is the average distance between pores in the direction of the char recession. It is determined by the number density and size of the pores dispersed in the char matrix. The expression can be obtained from some of the relations in stereology [17].

Consider a matrix in which particles of another phase (α -phase) are randomly distributed (the α -phase is the pores in a coal matrix in our discussion). For this system, we define a spatial parameter called the *mean free distance*, λ . The *mean free distance* is a mean edge-to-edge distance, which represents the *uninterrupted* inter- α -particle distance through the matrix averaged between all possible pairs of isolated α -particles. The distance can be expressed as follows [4]:

$$\lambda = \frac{1 - (V_V)_\alpha}{N_L} \quad (4)$$

where $(V_V)_\alpha$ and N_L are the volume fraction of α -phase, and the number of interceptions of particles per unit length of test line, respectively. The relation derives from the fact that the number of interceptions with α -particles is the same as the number of interceptions with the matrix. Thus the lineal fraction occupied by the matrix is λN_L , which is also equal to its volume fraction, $1 - (V_V)_\alpha$. Putting in another way, the mean distance between centers of features (or particles) is the inverse of the number of interceptions of features per unit length of test line, i.e., $1/N_L$. Now, in order to get the mean edge-to-edge distance, the mean traverse length, $1/N_L$, has to be adjusted with the volume fraction occupied by the feature, thereby getting

the equation (4). For particulate systems,

$$S_V = 2P_L \quad (5)$$

$$P_L = 2N_L \quad (6)$$

where S_V , P_L , and N_L are the surface area of particles per unit volume of the sample, the number of intersections of particles per unit length of test line, and the number of interceptions of particles per unit length of test line, respectively. Equation 5 holds regardless of the shape and size of the objects. On the other hand, equation (6) is true only for particulate systems, in which particles are randomly distributed in a matrix. (For space-filling grains systems, $P_L = N_L$.) From eqns 4, 5, and 6, we get

$$\begin{aligned} \lambda &= \frac{1 - (V_V)_\alpha}{\frac{1}{4}(S_V)_\alpha} \\ &= [4 \frac{(V_V)_\alpha}{(S_V)_\alpha}] \frac{1 - (V_V)_\alpha}{(V_V)_\alpha} \\ &= [4 \frac{(V_V)_\alpha / N_V}{(S_V)_\alpha / N_V}] \frac{1 - (V_V)_\alpha}{(V_V)_\alpha} \\ &= [4 \frac{\bar{V}_\alpha}{\bar{S}_\alpha}] \frac{1 - (V_V)_\alpha}{(V_V)_\alpha} \quad (7) \end{aligned}$$

$$= \bar{L}_3 \frac{1 - (V_V)_\alpha}{(V_V)_\alpha} \quad (8)$$

where $\bar{V}_\alpha$ and $\bar{S}_\alpha$ are the average volume and the average surface area per particle, respectively. Here, $\bar{L}_3$ is the mean intercept length [17], which is the average length of the intercepts when test lines are passed through an α -phase particle at all possible locations and angles. The mean intercept length for mono-sized spheres of radius r is $4r/3$.

The separation length scale, L_s , is simply the mean free distance between pores. Assuming uniform pore size, the distance can be expressed in terms of the porosity,

ϕ , and pore radius, r_p , i.e.,

$$L_s = \frac{4}{3} r_p \frac{1 - \phi}{\phi} \quad (9)$$

For a given pore volume fraction, the separation distance increases as the pore size increases (or as the number of pores decreases). For given pore size, the separation distance increases as the porosity decreases. For small porosity, the separation distance becomes simplified as follows:

$$L_s \sim \frac{r_p}{\phi} \quad (10)$$

Coalescence Length Scale, L_c

The coalescence length scale, L_c , is the distance a surface ash particle travels along with the receding char surface before it collides and coalesces with a mineral inclusion. A collision occurs between a surface ash particle (A) and mineral inclusions (B) whenever the distance between centers becomes as small as $d_{AB} = r_A + r_B$. Let us imagine a sphere of radius d_{AB} to be circumscribed about the center of A. Whenever the center of an inclusion (B) comes within this sphere, B immediately coalesces with A. When a surface ash particle recedes, it sweeps a cylindrical volume of the char the base of which is the projected area of this imaginary sphere onto the char surface. The coalescence length scale, L_c , can be obtained by calculating the height of the cylinder which overlaps with one mineral inclusion. An analogy to this analysis is found in the calculation of the mean free path of gas molecules.

Consider a cylindrical sweeping volume of height, L_c , with the radius of the base, $2r_m$ (Figure 3-6). From our definition of the coalescence length scale, the number of centers of (mono-sized) mineral inclusions contained in the cylinder is one, i.e.,

$$[\pi(2r_m)^2 L_c] \cdot N_V = 1 \quad (11)$$

where N_V is the number density of mineral inclusions (i.e., number of inclusions per

B-6067

Figure 3-6. Illustration of the coalescence length scale. Spheres in the figure represent mineral inclusions embedded in the char particle. The surface ash particle (top, closed sphere) sweeps the full length of L_c until it coalesces with a mineral inclusion (sphere in the bottom face of the cylinder). Mineral inclusions whose centers are in the cylindrical volume are incorporated to the sweeping ash particle.

volume of char). Therefore,

$$L_c = \frac{1}{4\pi r_m^2 N_V} \quad (12)$$

The number density of the mineral inclusions in the above relation is replaced by its volume fraction, θ , using the following relation:

$$\theta = \frac{4}{3}\pi r_m^3 N_V \quad (13)$$

From equations 12 and 13, the coalescence length scale is

$$L_c = \frac{r_m}{3\theta} \quad (14)$$

Given the inclusion radius, the coalescence length scale increases as the volume fraction, θ , decreases. Given the mineral volume fraction, the coalescence length scale increases as the mineral inclusion size increases. At fixed mineral volume fraction, the number of inclusions increases as its radius decreases, the distance between inclusions, therefore, decreases and hence the decrease of the coalescence distance.

Ash Growth Number, Λ

From equations 9 and 14, the parameter for ash growth, Λ , becomes:

$$\begin{aligned} \Lambda &\equiv \frac{L_s}{L_c} \\ &= \left(\frac{4r_p}{3} \frac{1-\phi}{\phi} \right) / \left(\frac{r_m}{3\theta} \right) \\ &= 4 \frac{r_p}{r_m} \cdot \frac{1-\phi}{\phi} \cdot \theta \end{aligned} \quad (15)$$

When the porosity is small, the equation (15) is simplified as

$$\Lambda = 4 \left[\frac{r_p}{r_m} \right] \cdot \left[\frac{\theta}{\phi} \right] \quad (16)$$

equation (16) is composed of two groups. The first is the ratio of the sizes of pores and inclusions. The second is the ratio of the volume fractions of pores and mineral inclusions. The simple and important physical meaning of the parameter, Λ , is that it gives the average number of mineral inclusions a surface ash particle encounters before it gets separated. For example, when $\Lambda < 1$, mineral inclusions never get a chance to coalesce with each other. On the other hand, when $\Lambda \geq 1$, a mineral inclusion, after exposed to the char surface, scavenges Λ mineral inclusions on the average before it gets separated. The final ash size is, therefore, related to the parameter, Λ , as will be shown in the next section.

Transient and Final Ash Size

The same "cylindrical sweeping volume" type of analysis can be carried out again for the calculation of the surface ash size as a function of time (or conversion).

Consider a surface ash particle of radius r_m sweeping down the char volume, and construct a cylinder of height z ($0 \leq z \leq L_s$) and radius $2r_m$. Since all mineral inclusions with their centers in the cylindrical volume coalesce to form one spherical particle of radius r_{ash} , we can get the following relationship:

$$\frac{4}{3} \pi r_{ash}^3 = \frac{4}{3} \pi r_m^3 \cdot [\pi (2r_m)^2 z] \cdot N_V \quad (17)$$

or

$$\begin{aligned} r_{ash}^3 &= (4\pi r_m^2 N_V z) r_m^3 \\ &= \left(\frac{4}{3} \pi r_m^3 N_V \cdot \frac{3}{r_m} z \right) \cdot r_m^3 \end{aligned}$$

$$\begin{aligned}
&= \left(\frac{3\theta}{r_m} z \right) \cdot r_m^3 \\
&= r_m^3 \left(\frac{z}{L_c} \right)
\end{aligned} \tag{18}$$

or

$$\begin{aligned}
r_{ash} &= r_m \left(\frac{z}{L_c} \right)^{1/3} \\
&= r_m \left(\frac{L_s}{L_c} \right)^{1/3} \cdot \left(\frac{z}{L_s} \right)^{1/3} \\
&= r_m \Lambda^{1/3} \cdot \left(\frac{z}{L_s} \right)^{1/3}
\end{aligned} \tag{19}$$

From equation (18), it is found that the average volume of the surface ash increases proportionally with the distance the reaction front moves down, i.e., with the conversion. Since the surface ash particle gets separated after L_s , the surface ash reaches its average final ash size at $z = L_s$. This average final ash size obtained from the equation (19) is

$$\bar{r}_{ash,f} = r_m \Lambda^{1/3} \tag{20}$$

Equations 19 and 20, in fact, underestimates the actual size. They are derived assuming that the surface ash particle sweeping the char volume does not grow in size even after the incorporation of the mineral inclusions in the sweeping volume. But, since the particle actually grows in size, the volume the particle sweeps (or the number of mineral inclusions the particle scavenges) increases. The actual system, therefore, is expected to deviate from the size predicted by equations 19 and 20.

Ash Growth Number in Spherical Char Configuration

Separation Length Scale, L_s

The main difference of the spherical from the planar char configuration is that the continuous increase of the reaction front curvature brings surface ash particles closer to each other. As a result, the coalescence of ash particles is enhanced as the char reaction proceeds. Since the separation length scale is the average edge-to-edge distance between pores in the direction normal to the char surface, the expression for the separation length scale in the planar char configuration also holds in the spherical configuration. We use equation (9).

Coalescence Length Scale, L_c

In this section we derive the coalescence length scale for the early stage of combustion. The coalescence length scale is again defined as the radial distance a surface ash moves until it encounters an inclusion. It is obtained from the volume of char whose inclusions end up being coalesced to the sweeping surface ash particle. This volume is no longer cylindrical due to the changing curvature of the reaction front. In the spherical configuration, all surface ash particles move radially towards the center of the char. The volume is a conical piece of a shell of the char which is defined by the projected images of an imaginary sphere.

Consider a char particle in Figure 3-7 of radius R_c with mineral inclusions of radius r_m . Suppose after combustion the radius of the char has reduced to ρ . Now we would like to look at the volume of the char whose mineral inclusions end up being scavenged to the surface ash of radius equal to that of the initial mineral inclusion, r_m . Let us first imagine a sphere of radius $2r_m$. Then we project this sphere onto the char surface of radius ρ . The projected image is now projected back to the initial char surface of radius R_c . We now have two cap-shaped projected images with the same solid angle. Finally we can construct a volume bound by

B-6066

Figure 3-7. Illustration of the coalescence length scale for spherical char configuration. Char particle with mineral inclusions is shown in 2- (bottom) and 3-dimensional space (top). A surface ash particle (open circle with an asterisk, bottom figure) sweeps a conical volume of the char shell as the char radius decreases from R_c to ρ with the progress of the reaction. Mineral inclusions (closed circles, bottom figure) in the volume are incorporated to the sweeping ash particle. Unreacted core of the char is shaded.

the two caps, which is a conical piece of a char shell. The mineral inclusions in the volume end up in the surface ash of radius r_m . By checking the number of inclusions in the volume, we can calculate the coalescence distance, L_c .

The volume of the conical piece of the shell, V_c , is obtained by calculating the solid angle of the projected area of an ash particle onto the char surface. It is the volume of the shell times the fraction of the solid angle of the caps. The solid angle of the projected area of a sphere with radius $(2r_m)$ is $4\pi r_m^2/\rho^2$, where ρ is the inner radius of the shell. The volume of the shell is $\frac{4}{3}\pi(R_c^3 - \rho^3)$. Therefore, the volume, V_c , is

$$\begin{aligned} V_c &= \frac{4}{3}\pi(R_c^3 - \rho^3) \left[\frac{4\pi r_m^2/\rho^2}{4\pi} \right] \\ &= \frac{4}{3}\pi r_m^2 \frac{R_c^3 - \rho^3}{\rho^2} \end{aligned} \quad (21)$$

Now, by the definition of L_c , there is one inclusion in the volume V_c . Therefore,

$$\begin{aligned} 1 &= V_c \cdot N_V \\ &= \left[\frac{4}{3}\pi r_m^2 \frac{R_c^3 - \rho^3}{\rho^2} \right] \cdot \left[\frac{\theta}{(4/3)\pi r_m^3} \right] \\ &= \frac{R_c^3 - \rho^3}{\rho^2} \cdot \frac{\theta}{r_m} \end{aligned} \quad (22)$$

The coalescence length, L_c , can be determined by equation (22) and from the relation, $L_c = R_c - \rho$. Assuming $R_c \gg L_c$, the above relation is simplified as

$$L_c = \frac{r_m}{3\theta} \quad (23)$$

which is identical to the equation (14) for the planar configuration. The coalescence distance will, of course, vary depending on the position of the surface ash particle being considered. But the expression (equation (23)) serves enough for our purpose.

Ash Growth Number

Equations 9 and 23 give the same ash growth number as that of the planar configuration:

$$\Lambda = 4 \frac{r_p}{r_m} \cdot \frac{1 - \phi}{\phi} \cdot \theta \quad (24)$$

Although this is true only for $R_c \gg L_c$, this relation can be used at least for qualitative analysis on the combustion performance and ash formation behavior of coals.

Transient Ash Size

Consider the conical volume of the shell associated with a surface ash particle of radius r_{ash} on the char surface of radius ρ . Its volume, $V_{c,\rho}$ is,

$$V_{c,\rho} = \frac{4}{3} \pi r_{ash}^2 \frac{R_c^3 - \rho^3}{\rho^2} \quad (25)$$

Since all inclusions in the volume $V_{c,\rho}$ end up in the surface ash of radius r_{ash} , and assuming the conservation of the ash volume,

$$\begin{aligned} r_{ash}^3 &= \left[\frac{R_c^3 - \rho^3}{\rho^2} \cdot \frac{r_{ash}^2}{r_m^2} \frac{\theta}{r_m} \right] r_m^3 \\ &= \frac{R_c^3 - \rho^3}{\rho^2} r_{ash}^2 \theta \end{aligned} \quad (26)$$

Therefore,

$$r_{ash} = \frac{R_c^3 - \rho^3}{\rho^2} \theta \quad (27)$$

or in terms of the dimensionless variable, $\bar{\rho} = \rho/R_c$,

$$r_{ash} = \left(\frac{r_m}{3} \right) \left(\frac{R_c}{L_c} \right) \frac{1 - \bar{\rho}^3}{\bar{\rho}^2} \quad (28)$$

The equation (28) is valid only for an intermediate stage of combustion where the growth is mostly due to the scavenging of the mineral inclusions embedded in the char. The stage for this scavenging growth (or the growth by the addition of mineral inclusions onto the surface ash particles) is further discussed in the parametric study section.

3.2.4 Scaling of the Ash Particle Size Distribution

The self-affine nature of the ash mass distributions obtained from simulations at different conditions strongly suggest the possibility of the scaling of the distributions. An attempt was made to scale the final ash particle size distributions (psd) by applying the scaling concept of the percolation theory.

If a function $F(x)$ has the property

$$F(x) \simeq b^{-H} F(bx) \quad (29)$$

it is called to be self-affine, where $H > 0$ is some exponent [18]. equation (29) expresses the fact that the function is invariant under the following rescaling: shrinking along the x axis by a factor of $1/b$, followed by rescaling of values of the function (measured in a direction perpendicular to the direction in which the argumentum is changed) by a different factor equal to b^{-H} . In other words, by shrinking the function using the appropriate direction-dependent factors, it is rescaled onto itself. For some deterministic self-affine functions this can be done exactly, while for some random functions the above considerations are valid in a stochastic sense (expressed by using the sign $\simeq$).

The scaling approach with the self-affine nature was taken by many researchers in a variety of dynamical processes [2, 11, 19, 15, 20, 1]. Dynamic scaling of the droplet growth with homogeneous [2] and heterogeneous [11] nucleation was

successfully carried out adopting the scaling concept. The process of droplet growth on a thin-film was described by assuming that the number of droplets of size s , at time t scales as

$$n_s \sim s^\tau f(s/S(t)) \quad (30)$$

where $S(t) (= \sum s^2 n_s(t) / \sum s n_s(t))$ is the mean droplet size, and $f(x)$ the scaling function. The mean droplet size increases with time, i.e., $S(t) \sim t^z$. By using the above relations and the definition of the mass density of the system, they get relations between exponents. From the computer simulation, the exponent z is obtained, and is used for other exponents. The simulation results were plotted according to the equation (30), and showed that the scaling function, $f(x)$, exists.

Sahimi and Tsotsis [15], in their char combustion simulation work, also followed the same approach and mentioned that the evolution of fragment size distribution can be described by hypothesizing that a dynamic scaling of the following form governs the evolution of the fragment size distribution:

$$n_s \sim t^{-w} s^{-\tau} f(s/t^z) \quad (31)$$

where n_s is the number of fragments (per network site) of s sites, and w, z and τ are dynamical exponents. These exponents are universal and do not depend on the microscopic details of the system, e.g., the pore size distribution of the char particle.

Sharing the same concept of scaling, we scale the ash particle size distributions with the ash growth number, Λ . The analogy is that while the average size of the droplets, S , is directly related to the time elapsed, t , in the droplet growth on thin-film, the average size of the flyash particles in our system is closely related to the ash growth number, Λ (e.g., equation (20)). The assumption we make for our system, which is equivalent to equation (30), is

$$n_s(\Lambda) \sim s^{-\tau} f(s/S(\Lambda)) \quad (32)$$

where τ is an exponent that is determined later. The mass mean size increases with the ash growth number, Λ :

$$S(\Lambda) \sim \Lambda^1 \quad (33)$$

which is from equation (20). Now we define the mass density, ϱ , as the mass of the mineral matter per volume of the system. By the definition,

$$\begin{aligned} \varrho &= \sum s n_s(\Lambda) \\ &\sim \int s^{1-\tau} f(s/S(\Lambda)) ds \\ &\sim S^{2-\tau} \int x^{1-\tau} f(x) dx \\ &\sim \Lambda^{(2-\tau)} \end{aligned} \quad (34)$$

Also,

$$\varrho \sim \theta \quad (35)$$

$$\sim \Lambda \quad (36)$$

where θ is the volume fraction of the mineral matter. To get equation (36) from equation (35), we assumed that the mineral inclusion size, r_m , is constant. In comparing equation (34) with equation (36) we find

$$2 - \tau = 1 \quad (37)$$

or simply, $\tau = 1$. The scaling form, therefore, becomes

$$n_s(\Lambda) \sim s^{-1} f(s/S(\Lambda)) \quad (38)$$

The scaling function $f(x)$ is determined from a series of computer simulations. Test of the scaling form in equation (38) can be done by plotting the scaled quantity

$s \cdot n_s$ versus the scaled variable $s/S(\Lambda)$. Independent of whether or not equation (38) is valid, we get one curve of $s \cdot n_s$ versus $s/S(\Lambda)$ for every different simulation condition. If equation (38) is valid, however, these curves for different conditions all collapse into a single curve, the scaling function $f(x)$. The scaled quantity, $s \cdot n_s$, is the total mass of ash per initial char volume, m_s . equation (38) implies, therefore, that if the scaling function exists, the ash mass distributions collapse into a single curve when plotted versus the ash size scaled with the mass mean ash size. This similarity can be compared with the known similarity of all circles: if each circle is reduced in its radius by a factor proportional to the square root of its area, then all these different circles look the same. The scaling function, if it exists, and the ash growth number can provide qualitatively important information on ash formation during pulverized coal combustion.

Extension of the scaling concept to the continuously changing surface ash particle size distribution is expected to be possible as well, as the dynamic scaling of the droplets in a thin film was successfully carried out [2, 11].

3.2.5 Parametric Study of the Model

Planar Configuration

A parametric study was performed to compare the Monte Carlo simulation results with the analytical results. The simulation runs were made in a continuum char space with its length, width, and depth of 20, 20, and 200 μms , respectively. For each of the conditions, 20 runs were made and the average of these runs was taken. The simulation conditions and their resulting average surface ash size right before the completion of the combustion are listed in Table 3-4.

Monosized mineral inclusions and pores were assumed for the input data. For each simulation condition, the coalescence length, separation length, and the ash

Table 3-4. Input Conditions for Computer Simulation Runs

run number	1	2	3	4	5	6	7
porosity, $\phi_p, [-]$	0.04	0.08	0.04	0.08	0.04	0.02	0.02
mineral content, $\theta_m, [-]$	0.02	0.04	0.02	0.04	0.04	0.04	0.08
pore radius, $r_p, [\mu\text{m}]$	2	3	3	4	2	2	2
mineral radius, $r_m, [\mu\text{m}]$	1	1	1	1	1	1	1
separation length, $L_s, [\mu\text{m}]$	64	47	97	64	64	132	132
coalescence length, $L_c, [\mu\text{m}]$	17	8	16	8	8	8	4
ash growth number, $\Lambda, [\mu\text{m}]$	3.9	5.6	5.8	7.7	7.7	15.9	31.9

The dimensions of the planar char are: length = 20 μm ; width = 20 μm ; and depth = 200 μm .

growth number are also reported.

In Figure 3-8 the change of the average surface ash size is plotted versus the reaction depth, z , for each of the simulation conditions. The increasing trend suggests the possibility of scaling the curves. The data were replotted in Figure 3-8 using equation (19) in normal and log-log scales, respectively. As is shown in Figure 3-8, results of runs at different conditions all collapse into a single curve. The slope of the line in the lower figure of Figure 3-9 is $1/3$ as was predicted by equation (19). The results show a good agreement between the simulation and the analytical derivation.

The final average ash sizes predicted with the ash growth number, Λ , were compared with those from the simulation in Figure 3-10. These also show a good agreement. Here, we see the usefulness of the ash growth number, Λ . Given the mineral inclusion size (or its distribution), the mineral content, the pore size (or its distribution), and the pore volume fraction, we can predict the average ash particle size. The size distribution can also be obtained from the scaling argument described earlier.

The growth of the separated ash is shown in Figure 3-11. It exhibits the same trend as the growth of ash on the char surface. Due to the smaller ash particles separated earlier, the growth of the mass mean size of the separated ash is slower. But the average size of separated ash is not much different from that of the surface ash (Figure 3-12).

The final ash (separated) size distributions obtained from each condition were plotted on a log-log scale in terms of number density versus ash size in mass (Figure 3-13). The number distributions increase with the ash size s at first and then decrease. When plotted in terms of the total mass of ash size s ($s \cdot n$, or m_s) and the ash size s , the distributions show a clear trend that as the ash number, Λ , increases, the distributions become broader while maintaining similar shapes. In other words, the distribution curves look as if they are stretched far to the larger ash size range as the ash growth number, Λ , increases. This self-affine nature leads us to the scaling of the distributions as discussed earlier. As was discussed in the previous

B-6065

Figure 3-8. Growth of average surface ash size r_{ash} with the reaction depth z . Runs were made on a planar char configuration at different conditions listed in Table 1. The ash growth numbers for each simulation conditions are listed in the legend in parenthesis.

Figure 3-9. Growth of average surface ash size rescaled with mineral inclusion size (r_{ash}/r_m) with the reaction depth rescaled with the separation length (z/L_s). Simulation runs were made on a planar char configuration. Results were replotted based on the equation (19). The slope of the line in the log-log scale is 1/3 as was predicted by equation (19) (lower figure) .

B-6074

Figure 3-10. Comparison of average surface ash sizes from simulation with those of analytically predicted. Mass mean ash size was obtained from the complete conversion of the char in planar configuration.

B-6075

Figure 3-11. Growth of mass mean size of the separated ash r_{ash} with the reaction depth z . Results were obtained from 20 runs were made on a planar char configuration at different conditions listed in Table 1. The ash growth numbers for each simulation conditions are listed in the legend in parentheses.

B-6076

Figure 3-12. Comparison of the growth of the mass mean size of separated ash with that of the surface ash. Separated ash size is smaller through the entire growth range. Refer to Table 1 for simulation condition.

Figure 3-13. Final ash number distributions for simulations on planar char configuration. The distributions are plotted in terms of the number density, n_s ($=$ [absolute number of ash of size s] / [initial number of inclusions]) and the ash size in mass unit.

section on scaling, the ash mass distributions were rescaled with the mass mean size of surface ash (which is not much different from the mean mass size of separated ash). The rescaled distributions, indeed, collapse into a single curve as is shown in Figure 3-14, which is the scaling function $f(x)$. The scaling function is approximately log-normal.

In order to answer for the question as to where the final ash particle size distribution resides between the two extreme cases (i.e., one ash per coal or one ash per inclusion), a simple analysis and simulation were carried out for bituminous coals in planar configuration. A typical U.S. bituminous coal has about 15 wt% (or ~ 8 vol%) of mineral content. Assuming average size of mineral inclusions of $1\text{ }\mu\text{m}$, the coalescence length, L_c , is approximately 4.17 from equation (14). From equation (18), the wall thickness required for the growth of the surface ash to twice the size of the mineral inclusion is $z = 2^3 \cdot L_c = 2^3 \cdot (4.17) = 33.4\text{ }\mu\text{m}$. Computer simulation of 50 runs was made for the case on a $20 \times 20 \times 100\text{ }\mu\text{m}$ continuum space assuming monosized mineral inclusions of radius $1\text{ }\mu\text{m}$. The simulation result for this case is shown in Figure 3-15, and agrees well with the calculated value. One thing to notice is that as the reaction depth increases, the average surface ash size from simulation deviates further away from the calculated value (solid line in Figure 3-15). This is, as was previously mentioned, due to the assumption made when equation (19) was derived. Namely, the surface ash was all taken to be points without volume. Obviously, since the surface ash particles have volumes, they continually increase in size. This enhances the coalescence between neighboring particles in addition to the incorporation of the mineral inclusions to them.

The ash size distribution on the char surface is also shown in Figure 3-16. The largest ash particle obtained after $30\text{ }\mu\text{m}$ of char layer removal was approximately $2.5\text{ }\mu\text{m}$ in radius. The surface ash particle size distributions were scaled using an

B-6078

Figure 3-14. Scaling of mass distributions of final ash. Upper figure shows the ash mass vs. ash size in mass, s , while the lower figure shows the ash mass vs. ash size reduced by the average mass/ S .

B-6079

Figure 3-15. Growth of the average surface ash radius obtained from the computer simulation of a typical bituminous coal. The average surface ash size doubles at the char depth of $30 \mu\text{m}$. The line drawn in the lower figure is the prediction obtained from equation (11).

B-6080

Figure 3-16. Surface ash particle size distributions obtained from the simulation of a typical bituminous coal of 8 vol% mineral content. Lower portion shows the distributions scaled by the equation (39). Development of another mode is observed.

equation similar to equation (38):

$$n_s(z) \sim s^{-1} f(s/S(z)) \quad (39)$$

The scaling result is shown in the lower portion of Figure 3-16, and shows an interesting feature developing as the reaction proceeds: the magnitude of the peak near $s/S = 1$ slowly decreases while another mode is beginning to develop near $s/S = 0.1$. As will be discussed in the following chapter, the bimodality can arise when the ash collision frequency (or the ash number density) is very high.

In conclusion, the result indicates that the final ash particle size distribution for swelling coals with wall thickness less than $10 \mu\text{m}$ is predicted about the same as that of the mineral inclusion size distribution. In other words, one ash particle per mineral inclusion is a good approximation for all practical purposes of swelling bituminous coal combustion. This is more so as other factors like the variation of mineral content from particle to particle become more important.

Spherical Configuration

A series of simulations was carried out with spherical char particles to investigate the ash growth behavior. A non-porous, spherical char particle was constructed for simulation in order to first find out where the major ash growth takes place. Monosized, $1 \mu\text{m}$ -radius mineral inclusions were distributed randomly throughout the $45\text{-}\mu\text{m}$ -radius char particle, with its mineral content of 8 vol%. Ten runs were made for the simulation condition and were averaged to obtain the final data.

The mass mean surface ash particle size was plotted in Figure 3-17 against the conversion of the char particle. As shown in Figure 3-17, surface ash grows rapidly in the early stage of conversion. After about 10 % of conversion, surface ash size plateaus and increases rather slowly. As the conversion reaches about 90 %, the surface ash size takes off once again and grows to its final size in a rapid manner.

B-6081

Figure 3-17. Growth of surface ash with conversion on a non-porous char. Three distinct stages of ash growth are shown in the figure. In the early and final stage of conversion, the growth is rapid mainly by the touching coalescence among the surface ash particles. In the intermediate stage, the growth slows down, and is mainly by the addition of the mineral inclusions onto the existing surface ash particles. The dotted curve is from equation (27), which accounts only for the growth by addition of mineral inclusions onto a surface ash particle. Initial char radius was $45\text{ }\mu\text{m}$, and the mineral content was 0.08. (spherical configuration)

In the early stage of conversion, mineral inclusions begin to be exposed to the char surface and form surface ash particles. A small change of curvature by conversion brings these mineral-inclusion-sized surface ash particles close together, and initiates a rapid coalescence among them. This rapid growth continues until it levels off. This can be understood by considering two closely neighbored surface ash particles. Coalescence of two identical surface ash particles to a single particle increases the volume of the final ash particle by a factor of two when it is compared with its parent ash particles. The surface ash radius increase in this case is by a factor of $\sqrt[3]{2}$. In terms of the char surface area occupied by ash particles, on the other hand, coalescence actually reduces its occupied surface area by a factor of $1/\sqrt[3]{2}$. Since the surface area occupied by ash particles is closely related to the degree of coalescence, this reduction of occupied surface area leads to the reduction of the coalescence probability among surface ash particles. The rapid coalescence in the early stage, in other words, effects having surface ash particles grow to larger particles, and at the same time, having them relatively apart from one another. After growth to a certain size, therefore, ash particles become far enough so that any further major coalescence does not occur for a while.

In the intermediate stage of conversion, the ash grows fairly slow because the growth is not by coalescence between surface ash particles, but mainly by addition of mineral inclusions onto the already existing surface ash particles. As the conversion proceeds, surface ash particles recede along with the receding char surface. Those mineral inclusions buried under the surface ash particles are scavenged by them. This growth by addition of inclusions continues until they are grown large enough so that another major coalescence among them is possible.

As the conversion draws near to the completion, surface ash particles become close to one another and start to coalesce with one another. This coalescence is mainly due to the rapid change of char radius of curvature with conversion.

The major growth of surface ash particles in the initial and final stages results

in an inflection point in the intermediate stage of conversion. This inflection point was predicted also by Kerstein [10] in the modeling work with a population balance model applied for a two-dimensional case.

The solid curve shown in Figure 3-17 is from equation (27), which accounts only for the growth by addition of mineral inclusions onto a surface ash particle. Its functional behavior compares with the growth of surface ash in the intermediate stage.

The next question was whether the mineral inclusion size changes the ash growth behavior. Equation (27) shows that for the *intermediate* stage of ash growth, the mineral content, θ , and the char radius, R_c , are the only parameters that change the ash growth behavior, and the average ash radius is independent of the mineral inclusion size, r_m . Simulation was carried out changing the size of mineral inclusions from $0.5 \mu\text{m}$ to $1 \mu\text{m}$. The mineral content and the initial char size were fixed at 0.02, and $45 \mu\text{m}$, respectively. As is shown in Figure 3-18, there was no significant difference in its growth behavior between the two conditions. This is true throughout the conversion. This means that both the growth by touching coalescence between surface ash particles and the growth by addition of inclusions are independent of the mineral inclusion size.

A set of computer simulations was carried out with spherical char particles of initial radius of $45 \mu\text{m}$ in order to answer some of the questions asked for planar configuration. The simulation conditions were the same as those for the simulations in planar configuration as listed in Table 3-4. For each condition, results are averaged over ten runs.

As shown in the previous section, the ash growth number, Λ , is an appropriate parameter for the prediction of the average radius (or the degree of coalescence) for chars of planar configuration. This may not be necessarily true for the spherical configuration, because the ash growth number does not account for the touching coalescence. In order to see the functional dependence of ash size on the ash growth

B-6082

Figure 3-18. Effect of mineral inclusions on ash growth behavior. Only the mineral inclusion sizes for the two simulation conditions are different. The mineral content was fixed at 0.02, and the initial char radius was 45 μm for both cases.

number, the mass mean ash radii of surface ash and separated ash particles were plotted against the ash growth number, Λ . Figure 3-19 shows a fluctuation at small Λ 's, but as Λ increases the ash size follows a linear increase. The trend is again that the mass mean radii of surface ash and separated ash increase approximately with the ash growth number to the one third power, i.e.,

$$\bar{r} \sim \Lambda^{1/3} \quad (40)$$

In Figure 3-20, the ash mass distributions, m_s , for the seven cases were plotted against the ash size in mass, s . One of the interesting features was that the distributions are bimodal with a peak in the vicinity of $s/S = 0.01$. The mass fraction of the peak was about 0.02 with the rest of the mass fraction in the peak next to it. The scaling of the distributions was attempted using the equation (38). The results are shown in Figure 3-20.

3.2.6 Summary

A continuum model was developed in a three-dimensional space. The model follows the ash formation and growth history. The continuum model is different from our previously developed percolation model in that the continuum model approaches the process of residual ash formation from the coalescence point of view whereas the percolation model views the process from the char fragmentation point of view. In the percolation model the char fragmentation was handled efficiently by keeping track of the connectedness of a cluster of char sites. In the continuum model, on the other hand, ash coalescence was handled with more flexibility by making an assumption that the separation of surface ash particles from their parent char particle takes place when they encounter pores.

Analytical expressions were formulated for the ash mass distributions and aver-

B-6083

Figure 3-19. Correlation between the ash growth number and the mass mean radii of separated and surface ash. At small Λ 's, fluctuation is observed. As Λ increases, the radii follow a linear trend.

B-6084

Figure 3-20. Ash mass distributions from simulations in spherical configuration. The scaled ash mass distributions (lower drawing) are not much different from the non-scaled distributions (upper drawing).

age ash size by considering a surface ash particle scavenging mineral inclusions in a cylindrical volume of char, and with the help of a stereological analysis on pore-to-pore distance. In the course of the model development, a dimensionless number called ash growth number was defined and utilized for the further analysis. The ash growth number represents in planar configuration the number of mineral inclusions a receding surface ash particle can scavenge before it gets separated from the parent char particle, and thus is used to predict the final ash size. A simulation study shows that when used with caution the ash growth number is an appropriate parameter even in spherical configuration for the prediction of the final ash size.

The self-affine nature of the ash mass distributions could lead to the successful scaling of a number of ash mass distributions. The ash growth parameter was again used for the scaling.

The results from the simulations in spherical configuration also showed a bimodality in the ash mass distributions. Incidentally the bimodality was observed from both the experiment and the percolation modeling.

In conclusion, the continuum model gives insight into the residual ash formation process. It captures most of the qualitative features that are observed from experiments, and has the capability of quantitatively predicting the residual ash particle size distribution.

3.2.7 References for Section 3.2

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SECTION 4

TASK 8 - ENGINEERING MODEL DEVELOPMENT

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4. TASK 8 - ENGINEERING MODEL DEVELOPMENT

4.1 Introduction

Progress on code development this quarter was made in three areas:

(1) implementation of a higher resolution initial coal particle size distribution, (2) more flexible treatment of the effects of limited mineral coalescence on flyash formation, and (3) a probabilistic treatment of the small mineral particle distribution on the smallest coal particles based on the Poisson distribution. Results generated with the latest version of the code for Illinois #6 are presented in Subsection 4.5.

4.2 Initial Coal Particle Size Distribution

The resolution of the initial coal particle size distribution in the current engineering model was restored to that of the original MIT version. At present the code can now handle up to 30 size bins of 10 μm width. This represents a significant increase in resolution over the 20 μm width used earlier (Quarterly Report No. 14). The only serious problem posed by this enhanced capability is the distribution of the large number of small mineral particles over the extremely numerous coal particles in the smallest size range (5 to 15 μm). The solution to this problem is discussed later.

4.3 Limited Coalescence Option

The limited coalescence option used until now (Quarterly Report No. 14) converted all mineral particles greater than a certain size into excluded mineral particles, thereby preventing them from coalescing with smaller mineral particles on the original coal particle. In the present code, the ability to discriminate among mineral particles on the basis of type as well as size has been added. In other words, the size at which exclusion begins can now be varied according to the mineral type. For example, we may choose to exclude only quartz particles greater than 20 μm and illite particles greater than 40 μm in a particular coal.

4.4 Distribution of Small Mineral Particles on Small Coal Particles

As mentioned earlier, the principal problem arising from the finer, 10 μm wide, size range now used in representing the coal particle size distribution is the increased number of coal particles in the smallest, 5 to 15 μm , size range. Particles of this size are generally the most numerous to begin with, and the increase occurs in order to conserve volume in the size range following the reduction of the characteristic particle volume by a factor of eight. (The characteristic size has decreased from 20 to 10 μm .)

As a result, a large increase in the code's memory requirements would occur if we continued to store separately each coal particle's mineral content as we do at present for the large coal particles and as is done in the original MIT code for all particles. At the same time, the increased number of small coal particles also results in a small value (often less

than one) for the average number of particles of each mineral type per small coal particle. This invalidates, for the smallest coal particle size range, the basis of our present technique for distributing small mineral particles. In this technique, the mineral particles are distributed in direct proportion to the mineral free volume of each coal particle. When applied to smaller numbers of larger particles generated using the coarser size ranges of the earlier distribution, the resulting average numbers of mineral particles per coal particle were high enough so that deviations could be ignored to a good first approximation.

Because of these consequences of the finer coal particle size ranges, a new methodology is needed for distributing the smallest mineral particles among the smallest coal particles. The new methodology relies primarily on the Poisson distribution and is based on the following statistical characteristics of the mineral particle distribution on small coal particles. These characteristics are:

- (1) Only mineral particles less than 10 μm can be placed on a small coal particle of 10 μm size. In terms of the characteristic mineral sizes used at present, only 2, 4, and 8 μm mineral particles are allowed.
- (2) The number of smallest coal particles is generally much greater than the number of 4 and 8 μm mineral particles placed on the smallest coal particles. Thus the chance of placing a second 4 μm mineral particle on a 10 μm coal particle already containing one 4 or 8 μm mineral particle is small. (Two 8 μm particles cannot fit on one 10 μm coal particle.)
- (3) The average number of smallest mineral particles (for all types) per 10 μm coal particle is generally in the range of 1 to 5. For example, for the distributions shown in Tables 4-1 and 4-2, the averages for Illinois #6 and San Miguel are about 1 and 3.7, respectively.

These characteristics are accounted for in the following new discrete mineral distribution procedure. The new procedure has three principal components:

- (1) The way in which all large mineral particles (i.e., those $> 2 \mu\text{m}$) are placed on the large coal particles (i.e., those $> 10 \mu\text{m}$) is unchanged. A large mineral particle is randomly selected and its placement on a randomly selected coal particle is attempted. If the coal particle is greater than 10 μm and the mineral particle volume does not exceed the mineral-free volume of the coal particle, the coal particle's mineral inventory is revised to include the new mineral particle. If the mineral particle is too large to fit, it becomes an excluded mineral particle.
- (2) If the selected coal particle lies in the 10 μm size class, all mineral particles larger than 8 μm are automatically excluded. All 4 and 8 μm mineral particles are assumed to fit, but the mineral compositions of individual 10 μm coal particles are not saved. Only the total numbers of 4 and 8 μm particles of

Table 4-1. Simulated Coal and Mineral Particle Distributions for Illinois #6

Coal Particle Size Distribution

Average Size (μm)	Input		Output	
	Volume Frac. (%)	Number Frac. (%)	Number	Volume Frac. (%)
10.00	16.10	81.571	154984	16.23
20.00	22.20	14.060	26713	22.38
30.00	14.70	2.758	5241	14.82
40.00	12.30	0.974	1850	12.40
50.00	8.30	0.336	639	8.36
60.00	6.40	0.150	285	6.45
70.00	5.20	0.007	146	5.24
80.00	3.20	0.032	60	3.22
90.00	2.40	0.017	32	2.44
100.00	2.00	0.010	19	1.99
110.00	1.60	0.006	12	1.67
120.00	1.20	0.004	7	1.27
130.00	0.50	0.001	2	0.46
140.00	1.20	0.002	4	1.15
150.00	1.00	0.002	3	1.06
160.00	1.00	0.001	2	0.86

Number of Inclusions of Each Size (μm) for Each Mineral Type

Mineral	2.0	4.0	8.0	16.0	30.0	60.0
Quartz	215389	40986	4543	543	19	0
Kaolinite	98826	13345	995	155	5	0
Illite	201330	22041	2023	133	8	0
Mix. Sil.	306030	37131	3258	306	16	2
Pyrite	76525	6407	1168	568	81	5
Calcite	22255	3019	363	197	24	5
Others	102037	1697	272	336	68	4
All min.	1022392	124626	12622	2238	221	16

Table 4-2. Simulated Coal and Mineral Particle Distributions
for San Miguel Lignite

Coal Particle Size Distribution

Average Size (μm)	Input		Output	
	Volume Frac. (%)	Number Frac. (%)	Number	Volume Frac. (%)
10.00	37.00	94.247	282741	39.89
20.00	14.00	4.458	13373	15.09
30.00	9.00	0.849	2547	9.70
40.00	7.00	0.279	836	7.55
50.00	4.00	0.082	245	4.32
60.00	3.00	0.035	106	3.23
70.00	3.00	0.022	67	3.24
80.00	2.00	0.010	30	2.17
90.00	2.00	0.007	21	2.16
100.00	1.00	0.003	8	1.13
110.00	2.00	0.004	11	2.07
120.00	1.00	0.001	4	0.98
130.00	0.50	0.001	2	0.62
140.00	0.50	0.000	1	0.39
150.00	0.50	0.000	1	0.48
160.00	0.50	0.000	1	0.58
170.00	0.50	0.000	1	0.69
180.00	0.50	0.000	1	0.82
190.00	1.00	0.000	1	0.97
200.00	1.00	0.000	1	1.13
210.00	1.50	0.000	1	1.31
220.00	1.50	0.000	1	1.50

Number of Inclusions of Each Size (μm) for Each Mineral Type

Mineral	2.0	4.0	8.0	16.0	30.0	60.0
Quartz	350641	110360	12334	1109	148	7
Kaolinite	127057	3299	843	190	19	5
Montmor.	990083	63563	16456	1787	184	11
Mix. Sil.	1030551	217607	39258	10394	1529	73
Pyrite	25205	2845	578	125	9	4
Others	287053	7043	1578	360	22	12
All min.	2810590	404717	71047	13965	1911	112

each mineral type placed are stored. If there are NTYPE mineral types, then after distributing all of the large mineral particles, there will, in general, be $2 \cdot \text{NTYPE} + 1$ classes of $10 \mu\text{m}$ coal particles. The number of coal particles in a class equals the number of mineral particles of a particular type and size (4 or $8 \mu\text{m}$) randomly selected for placement on a $10 \mu\text{m}$ coal particle. The final class contains all $10 \mu\text{m}$ coal particles with neither a 4 nor an $8 \mu\text{m}$ mineral particle. Since the probability of placing more than one large mineral particle on a $10 \mu\text{m}$ coal particle is small, all 4 and $8 \mu\text{m}$ mineral particles are assumed to reside on different coal particles.

- (3) Once the large mineral particles have been distributed, the smallest ($2 \mu\text{m}$) mineral particles are distributed among the $2 \cdot \text{NTYPE} + 1$ small coal particle classes using the Poisson distribution to determine the fractions of each class receiving 1, 2, etc. small mineral particles per coal particle. The statistical characteristics of this situation are ideally suited for the use of the Poisson distribution:
 - (i) There are a large number of trials N_i , the number of mineral particles of each type i .
 - (ii) There is a small probability p_α of successfully placing a single mineral particle of any type on any particular small coal particle. This probability is the ratio of the mineral-free volume of a $10 \mu\text{m}$ coal particle V_α to the total mineral-free volume V_{TOT} of the entire sample distribution.
 - (iii) The average number $\lambda_{i\alpha}$ ($= N_i p_\alpha$) of mineral particles of type i on a small coal particle is small.

To implement this scheme, the three primary probabilities P_α are first evaluated:

$$P_\alpha = \frac{V_\alpha}{V_{\text{TOT}}} \quad (4-1)$$

In the present version, there are three possible values for V_α : V_0 is the volume of a $10 \mu\text{m}$ coal particle, i.e., a particle with no large mineral inclusions; V_4 and V_8 are equal to V_0 minus the volume of either a 4 or an $8 \mu\text{m}$ mineral particle. With the values of p_α , the NTYPE values of $\lambda_{i\alpha}$ needed for each of the $2 \cdot \text{NTYPE} + 1$ classes of small coal particles are easily evaluated. Thus, in terms of the Poisson probability density, the probability of finding k_i small mineral particles of type i on a given small coal particle is given by the expression

$$P(k_i, \lambda_{i\alpha}) = \exp(-\lambda_{i\alpha}) (\lambda_{i\alpha})^{k_i} / k_i! \quad (4-2)$$

Because the number of mineral particles on a given coal particle is small, there is no possibility of filling the coal particle fully with mineral particles, and the probabilities for placing different mineral types are independent. Thus, the overall probability for finding k_1 particles of type 1, k_2 of type 2, k_3 of type 3, etc. is given by the product of the individual probabilities:

$$P_{TOT}(k_1, k_2, \dots, k_{NTYPE} | \alpha) = \prod_{i=1}^{NTYPE} P(k_i, \lambda_i | \alpha) \quad (4-3)$$

For each of the $2 \cdot NTYPE + 1$ classes of small coal particles, a set of P_{TOT} values is generated by varying the k_i values from 0 to some modest upper limit k_{max} . To date the value $k_{max} = 4$ has been found to give satisfactory results. Combinations of k_i values that yield $P_{TOT} < 0.001$ are rejected, and the surviving P_{TOT} values are renormalized. The remaining satisfactory combinations comprise a set of subclasses into which the original number of coal particles in the class have been divided. The number of coal particles in each subclass and the associated mineral composition are stored to await distribution of organically bound inorganic matter and eventual processing into flyash particles.

Before proceeding to a discussion of some recent results employing the modified computer code the assumption of single particle occupancy by 4 and 8 μm mineral particles will be examined a bit more closely. Consider first the numerical distribution data for Illinois #6 in Table 4-1.

The volume fraction of 10 μm coal particles is about 16.2%. Therefore, we expect that same percentage of the total number (137248) of 4 and 8 μm mineral particles to be placed on the smallest coal particles. Thus the average number of 4 and 8 μm particles per 10 μm coal particle is given by

$$\lambda = (0.162 \times 137248 / 154984) \approx 0.14 \quad .$$

With this value of λ , Eq. (2) can be used to estimate the probability $P(> 1)$ of finding two or more large mineral particles on a single 10 μm coal particle:

$$P(> 1) = 1 - P(1, \lambda) - P(0, \lambda) = 0.009 \quad .$$

Therefore, since less than 1% of the smallest coal particles will be expected to have more than one large mineral particle on them, the assumption of single occupancy for Illinois #6 is very good.

When a similar exercise is performed for the San Miguel data in Table 4-2, the probability for multiple occupancy is much higher, about 15%. Thus, in this case, the single occupancy assumption will lead to observable errors of in the small end of the predicted flyash distribution. The possibility of multiple occupancy can be readily accounted for by

using the Poisson distribution in a manner similar to that just described for the smallest mineral particles. This work will be undertaken in the next quarter.

4.5 Model Predictions of Ash Size and Composition Obtained from Combustion of Illinois #6 Coal

Mineral analysis for Illinois #6 coal determined by CCSEM on a cross-sectioned coal sample is presented in Table 4-3. The data obtained from CCSEM do not correspond to the true mineral size distribution because the measurement constitutes randomly cut sections of the mineral inclusions. An inversion procedure described in Quarterly #15 is used to convert these measured values to a corrected mineral size distribution (Table 4-3), which is then used in the mineral matter transformation model. Most of the minerals in this coal are less than 40 μm in size, with silicates concentrated in the <10 μm range. Calcite levels for this coal are generally higher than for the other coals studied in this program. Pyrite and calcite inclusions are also generally >20 μm in size.

Table 4-3. Measured and Derived Mineral Size Distributions for Illinois #6

Mineral	Area % in Mineral Matter	Input Measured Area % for Each Size (μm)					
		2.0	4.0	8.0	16.0	30.0	60.0
Quartz	23.12	20.00	27.00	24.00	22.00	5.00	1.00
Kaolinite	7.01	29.00	29.00	18.00	21.00	4.00	0.00
Illite	11.56	35.00	29.00	21.00	11.00	4.00	0.00
Mix. Sil.	20.67	30.00	27.00	19.00	14.00	5.00	4.00
Pyrite	17.15	8.00	6.00	10.00	33.00	29.00	13.00
Calcite	7.80	8.00	6.00	7.00	25.00	21.00	32.00
Others	12.69	16.54	2.31	4.52	28.90	35.12	17.48
All minerals	100.00	21.00	19.00	16.00	22.00	14.00	8.00

Mineral	Volume % in Mineral Matter	Derived Input Volume Area % for Each Size (μm)					
		2.0	4.0	8.0	16.0	30.0	60.0
Quartz	23.12	18.27	27.49	24.37	23.32	5.44	1.11
Kaolinite	7.01	26.67	29.50	17.60	21.89	4.35	0.00
Illite	11.56	32.94	29.56	21.71	11.39	4.39	0.00
Mix. Sil.	20.67	28.36	27.85	19.55	14.67	5.13	4.44
Pyrite	17.15	7.65	5.79	8.44	32.87	30.82	14.41
Calcite	7.80	7.65	6.00	5.77	25.09	20.01	35.48
Others	12.69	15.62	2.07	2.66	26.28	35.08	18.29
All minerals	100.00	19.65	19.22	15.57	22.22	14.56	8.78

The first step in the mineral matter transformation model is to place the minerals in the coal particles in a random manner. Special cases for the distribution of smallest mineral size ($2\text{ }\mu\text{m}$) among the different coal particle sizes, distribution of the 2, 4, and $8\text{ }\mu\text{m}$ inclusions into the smallest coal particles ($5\text{ to }15\text{ }\mu\text{m}$), and the assignment of organically bound elements (calcium, sodium, etc.) have been discussed in Quarterly #14 and earlier in this section. Once the minerals have been appropriately assigned to the different coal particles, their transformation during combustion is modeled by including mechanisms in order of importance. The first mechanism considered is that of limited coalescence. Included minerals can coalesce with other inclusions within a coal particle and the extent of coalescence is a function of coal particle temperature during combustion, the size and composition of minerals, the time available for coalescence which corresponds to coal particle burnout times, and inter-inclusion distance which is related to the mineral loading in the coal. Higher combustion temperatures in conjunction with minerals that melt/soften (e.g., pyrite, clays) engender coalescence. So do large coal particles (longer burnout time) and higher ash loadings. In the model, the coalescence parameter is represented by a critical size for each mineral type. Inclusions at and below this size coalesce, and those above it form separate ash particles. As the model is developed further, guidelines with respect to the choice of critical sizes will be incorporated into the model.

For Illinois #6 coal, since a large number of the inclusions are small, hence included, coalescence is expected to dominate. Three cases with different choices of the coalescence parameters were considered (Table 4-4). The computed results for these three cases (Table 4-5) were compared with measured ash particle size and composition distribution.

Results shown in Table 4-5 indicate relative insensitivity to assuming coalescence of $16\text{ }\mu\text{m}$ and larger inclusions (i.e., cases 1 and 2) but significant differences between the extremely limited coalescence case and the other two. In particular, quartz inclusions, which are not allowed to interact with the clay minerals and pyrite in case 3, dominate the final ash spectrum, constituting almost 40 area percent of the total ash as silica-rich particles. In the following, when we compare the calculations to measured ash sizes and compositions we will

Table 4-4. Coalescence Parameter (mineral inclusion size below which coalescence occurs, in μm)

Mineral Type	Case 1	Case 2	Case 3
Quartz	≤ 8	All	2
Kaolinite	8	All	2
Illite	All	All	2
Mixed Silicate	All	All	2
Pyrite	16	All	2
Calcite	4	All	2
Others	All	All	2

Table 4-5. Ash Size and Composition Distribution (Area %)

Coalescence	Case 1 Partial	Case 2 Full	Case 3 Extremely Limited
<u>Size (μm)</u>			
2	7.4	7.6	6.6
4	18.9	19.3	17.5
8	33.6	33.6	43.9
16	27.1	25.2	23.6
30	10.7	11.7	7.0
60	2.3	2.7	1.5
<u>Composition</u>			
Si Al K	31.1	30.4	19.1
Si _ _	16.4	16.4	39.0
Si Al Ca	10.5	10.4	11.1
Si Al Fe	10.2	9.3	7.8
Si Fe Al	8.3	8.2	5.6
Fe _ _	5.2	4.7	6.8
Ca _ _	4.8	3.6	2.5
Si Al _	5.5	6.1	3.1
Fe Si Al	3.2	3.6	0.8
Others	4.8	7.3	4.2

see that partial or full coalescence options, as represented by cases 1 and 2, are more appropriate to describe the mineral matter transformations during the combustion of this coal.

Comparison of Model Predictions to PSIT and U. Arizona Data

Model predictions corresponding to the partial coalescence option (case 1) are compared with experimental data on ash size and composition distribution from PSIT and U. Arizona facilities. Figure 4-1 shows the measured and predicted overall size distributions. Errors are inherent in the measured mineral size distribution, which is used as input to the model, and in the measured ash size distribution. Further uncertainty is introduced during the inversion of the CCSEM mineral area distribution to a true volume distribution. Given these uncertainties, model predictions closely mirror the experimental results. The assumption of significant coalescence of minerals included within the coal particles is therefore appropriate.

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Figure 4-1. Ash Particle Size Distributions, as Measured by CCSEM, Generated by Combustion of Illinois #6 Coal at PSIT and UA, and Compared to Model Predictions

Figure 4-2 shows the ash composition distribution as determined by model predictions and in the two laboratory facilities. The ash composition is dominated by the coalescence of pyrite-derived inclusions with silicate minerals to form a range of iron-aluminosilicate composition particles and also by the interaction of organically bound calcium with the different silicate minerals. Consequently, silica-rich particles are lower in the ash (16 volume %) compared to quartz in the coal (24 volume %), and only a small fraction of iron-rich particles (5 volume %) are formed from pyrite (17 volume %) in the coal. Model predictions of the ash composition distribution agree quite closely with the measured data, again indicating that the important mechanism of coalescence has been well-represented in the calculations. The redistribution of two of the important basic elements (Ca and Fe) present in various minerals in coal among the different ash compositions is discussed next.

Behavior of Ca

Calcium is present in this coal in mainly two forms - calcite (CaCO_3) and organically-bound. The size distribution of calcite in the coal and that of Ca-rich particles in the ash as measured and as predicted by the model is shown in Figure 4-3. The figure illustrates the occurrence of calcite fragmentation for the larger inclusions which is not as yet included in the model. Note that the calcite size distribution is a cross-sectional area percent

B-5694

Figure 4-2. Comparison of Ash Composition Distribution for Illinois #6 Coal

which is close to the true volume percent if the inversion is performed. Hence the effect of fragmentation is exaggerated in the figure and would in reality be less if compared on a volume percent basis. Excluded calcite particles, during their flight through the combustion zone, decompose to CaO and release CO_2 . The thermal and mechanical stresses associated with this chemical reaction and gas release are responsible for particle break-up. At the other end of the size distribution, a significant discrepancy between the predicted and measured amount of fine CaO particles is noted. In the calculations, this results directly from the organically-bound calcium that has not interacted with other minerals. Organically-bound calcium in the coal is converted to sub-micron inclusions of CaO during the early stages of coal pyrolysis. Subsequently, it can be released from the coal particle either with the convective flow of the volatiles, or by vaporization. Both these release mechanisms which will contribute to mass in the sub-micron size range need to be incorporated in further extensions of the model.

The variation of individual particle composition illustrating the interaction of Ca with Al and Si is shown in triangular plots in Figure 4-4. Points clustered around the pure calcium apex indicate calcite decomposing to form calcium oxide without interacting with other minerals. CaO is fairly refractory (melting point = 2614°C) and large inclusions are therefore not expected to coalesce to any significant extent. The smaller inclusions and the

Figure 4-3. Calcium-Rich Particle Size Distribution (Illinois #6)

Figure 4-4. Calcium Interactions for Illinois #6 Coal

sub-micron CaO formed from the organically-bound calcium, however, will interact to form a range of calcium-aluminosilicate compositions. It is noted experimentally that a calcium-rich layer is formed on the glassy aluminosilicate ash, indicating the temperature and time during the combustion process is not sufficient to enable calcium to diffuse to the center of the ash particles. In the current model, the organically bound calcium is uniformly distributed within the ash particles. The model will be extended to incorporate the mechanism of forming calcium-rich surface ash compositions.

Behavior of Fe

Iron is present in this coal mainly as pyrite (FeS_2), illite, and mixed silicates. Pyrite present within the coal particle will decompose to pyrrhotite, melt and form an iron oxysulfide melt. Consequently, it has a greater propensity to coalesce with other included minerals than calcite. The extent of coalescence of pyrite with other minerals is evident in the triangular composition plot shown in Figure 4-5 and in the composition distribution (Figure 4-2). A range of iron aluminosilicate composition ranging from iron-rich (Fe Si Al) to a small amount of iron (Si Al Fe) are formed. Large pyrite grains on the other hand, often get released during coal grinding and behave in a different manner. They decompose to form pyrrhotite, and then oxidize to an oxysulfide melt, crystalline magnetite, and eventually hematite. During this process, some pyrite fragmentation occurs. Comparison of the size distribution of iron-rich particles (Fe _ _) obtained from calculations and

Figure 4-5. Iron Interactions for Illinois #6 Coal

measurements indicates that excluded pyrite fragmentation as a size reduction mechanism must be considered.

Addition of the aforementioned mechanisms into the model will be undertaken in the next quarter. The mechanisms include fragmentation of excluded calcite and pyrite, vaporization/release of organically-bound elements (Ca, Na, K) and surface enrichment of silicate ash resulting from interaction of organically-bound calcium.

Table 4-6. Size Distribution (Number %) of Fe-Rich Particles:
Model Calculations and PSIT Ash Data

Size (μm)	<2.5	2.5-5	5-10	10-20	20-40	40-80
Model	0	66	12	16.6	5.1	0.3
PSIT Ash	57.1	31.1	8.6	2.5	0.5	0.2

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