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**The partitioning of iron during the combustion of pulverized
coal**

Bool, Lawrence E., III, Ph.D.

The University of Arizona, 1993

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THE PARTITIONING OF IRON DURING THE COMBUSTION OF
PULVERIZED COAL

by

Lawrence E. Bool III

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMICAL ENGINEERING

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For the Degree of

Doctor of Philosophy

In the Graduate College

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THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

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SIGNED: Lawrence E. Reed III

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ABSTRACT

The presence of pyrite in coal has long been known to affect the slagging propensity of the coal when burned in industrial boilers. In particular it has been found that molten pyrite bonds very well to steel furnace tubes. In addition, it has been found that the amount of chemically bound iron greatly influences the slag contact angle and stickiness on steel heat transfer tubes.

The goal of this research, which is part of a larger project headed by the PSI Technology Company to study mineral matter transformations during combustion, is to explore and model the mechanisms dominating the fate of iron during combustion. To achieve this goal a well characterized suite of coals was burned in a 17kW downfired laboratory combustor. Fly ash was extracted from the flue gas and size classified. These ash samples were then subjected to a number of analytical techniques including Atomic Absorption Spectroscopy (AA), Energy Dispersive X-Ray (EDX), Computer Controlled Scanning Electron Microscopy (CCSEM), Transmission Electron Microscopy (TEM), and Mössbauer Spectroscopy to determine the ash bulk composition and morphology. Of these techniques, Transmission Electron Microscopy and Mössbauer, were instrumental in determining the iron-silicate interactions during combustion.

Utilizing the information gleaned from the fly ash analysis, and work in the literature,

it was possible to propose a pathway for iron interactions during combustion. A mechanistic model was then proposed to quantify the competition between processes governing iron oxidation/crystallization and those promoting iron-silicate mixing/reaction. This model described the partitioning of iron between chemically bound and physically bound phases. By utilizing kinetic parameters from the literature and fundamental transport phenomena, this model was able to successfully correlate data from several coals burned under a range of combustion conditions. The model can also be used to quantify the effect of combustion modifications and fuel property changes on iron partitioning.

Chapter 1

1. Introduction

One of the major problems encountered by utility companies utilizing coal fired boilers is the deposition of ash on heat transfer surfaces in the boiler. This ash, initially mineral matter contained in the coal, may subsequently fuse to form slag deposits that are extremely difficult to remove from the heat transfer surfaces. A host of problems are associated with these ash deposits including loss of heat transfer efficiency, increased maintenance costs, and increased boiler downtimes.

Several methods are currently used to predict the slagging propensity of a given coal based on the overall composition of the ash. These methods, including the slagging index (Gray and Moore, 1975), and the silica ratio (Raask, 1985), may predict (usually successfully) that a coal will cause slagging problems. However, many times coals that have been predicted to be benign, according to the traditional methods, are found to be severe slaggers. One possible reason for this discrepancy is the fact that the methods are based on the ash composition as a whole while neglecting the mineral matter distribution in the coal (Borio and Narciso, 1979, Borio and Levassuer, 1985), particularly the inherent (inside the carbon matrix) versus extraneous (outside the carbon matrix) mineral matter (Bryers, 1979).

Iron has long been known to play a major role in the initiation and fusing of ash

deposits. Most of the work performed to date has focused on the behavior of the extraneous iron species, primarily pyrites. The inherent pyrite, on the other hand, has been studied only on a qualitative basis and found to be a slag contributor in its own right.

1.1 Slag Induced Problems in Coal Fired Boilers

Many of the problems caused by slag formation in boilers are related to the loss of heat transfer efficiency and the corrosive nature of the deposits. For example, when deposits are formed they add a rather large heat transfer resistance to the boiler walls due to the relatively low thermal conductivity of the deposits (Richter et al., 1986). This, then, results in the boiler operating at a much lower efficiency than predicted in the design. The lower efficiency, in turn, requires either a larger fuel load to maintain the required steam rate, or a derating of the boiler.

The loss of heat transfer efficiency in some parts of the furnace can also cause catastrophic failure of the furnace tubes due to overheating. One study estimates that overheating accounts for 48.7% of all boiler failures (Metals Handbook, 1986). Mechanisms of failure due to overheating include ductile fracture, high temperature creep, carbide deposition, and high temperature fatigue (French, 1983, Plumbridge, 1987).

The slag deposits may also directly cause the boiler to fail. When the molten deposits in the upper part of the furnace are large enough, they may slough away from the walls and fall on to the tubes below, causing mechanical damage to the furnace.

Finally, the slag deposits have been shown to cause corrosion of the boiler tubes. This corrosion is often caused by reaction of the iron tubes with the slag mixture as proposed by Borio et al. (1977). The iron oxides and sulfides, often in conjunction with alkali species, react with the tube wall material. Thus, the tube wall material is slowly degraded until failure occurs.

As would be expected, boiler failures and derating are extremely expensive for the utilities involved. As an example, a senior engineer of the Pennsylvania Electric Company estimated that every day a boiler is not in operation costs \$250,000-\$350,000, in 1984 dollars (Austin et al., 1984). The major losses would be caused by the need to purchase power from other producers to meet the consumer demand. Although the cost of saved fuel helps to balance the operational losses, a large loss is still incurred by the power company. In addition to these operational losses are the costs incurred for increased maintenance and boiler tube replacement.

1.2 The Role of Iron in Slag Formation

It has long been known that coal mineral matter iron content, specifically as pyrite, has a strong effect on the slagging characteristics of a coal. This can be attributed to the effect of iron on a silicate melt and the ability of iron to initiate slag deposits.

Iron can be incorporated into slag deposits by either initiating the deposit, or by impacting and sticking to existing deposits. One investigator (Baxter and Mitchell, 1992) has also suggested that upon rapid oxidation of the pyrrhotite ($\text{Fe}_{0.877}\text{S}$, from the original pyrite) to iron oxide, an iron oxide fume is formed. This fume could conceivably deposit on the existing slag deposits as well.

Once incorporated into a alumina-silicate melt, iron has a large effect on the melting point and the viscosity of the system. Kalmanovitch et al. (1986), for example, showed that the liquidus temperature (or the temperature at which the first crystalline phases occur) tends to decrease with increasing iron content of the mixture. In addition, iron has the ability to act as either a weak acid or a weak base in a silicate melt (Vorres, 1979). As a weak acid, or network former, Fe^{3+} tends to enhance slag viscosity under oxidizing conditions. Under reducing conditions Fe^{2+} acts as a weak base, or network modifier, and reduces slag viscosity (Raask, 1985). Furthermore, as the sintering rate of an ash deposit is a strong function of viscosity (Raask, 1985), iron may serve to increase the sintering rate of existing deposits. It

has also been suggested that molten iron species, glasses and sulfides, play a role in the sintering of deposits (Nowak, 1990).

The iron contained within existing slag deposits, or in silicate melts, has also been studied to determine its effect on the stickiness of the melt. Austin et al. (1980), for example, noted that "addition of FeO to a coal ash reduces the sticking temperature from nearly 500°C to under 400°C". If the temperature is less than the sticking temperature, the particle will not stick to the substrate. "Incorporation of iron oxide in a glass was found to reduce the contact angle or enhance wetting on an iron substrate" (Adams, 1962). It was also determined that pyrite captured in a glass actually caused it to become more sticky than an equal amount of iron oxide (Abbot et al, 1985).

The ability of iron to initiate deposits has also been studied according to the dispersion (extraneous versus inherent) of the original iron in the mineral matter. The behavior of the extraneous iron (primarily pyrites) under combustion conditions has been studied in detail by a number of investigators utilizing a wide range of techniques (Asaki et al, 1985, Groves et al, 1987, Huffman et al, Jorgensen, 1981, Thorpe et al, 1987, Srinavaschar et al, 1989, and others). These investigators found that the pyrite initially decomposes to pyrrhotite, and possibly fragments, at relatively low temperatures (800-900 K). The solid pyrrhotite then oxidizes to magnetite until its melting temperature (1356 K) is reached. The pyrrhotite and the oxide then melt

and form a Fe-S-O melt. This melt continues to oxidize until oxidation is complete. The magnetite melt may then crystallize or further oxidize to hematite, depending on the combustion conditions. The iron sulfide melt (formed quickly under typical combustion conditions), and the Fe-S-O melt formed as the pyrrhotite oxidizes, is very sticky. Therefore the extraneous pyrite has been found to play a major role in slag deposit initiation, especially in the fuel rich zone around the flame (Reid, 1971, Raask, 1985, Bryers, 1976, Borio and Narciso, 1979).

For the same reasons that iron tends to exacerbate existing slag deposits (low melting points, high adhesion to steel surfaces), glasses formed from inherent iron and silicate mineral matter are suspected to be strong deposit initiators. Unfortunately the inherent iron has not been studied in detail. One investigating team, Abbot and Austin (1985), found that "microscopic analysis showed that the coal with the worst tendency for slag deposit formation contained pyrite and quartz or clays in intimate mixture". Another study suggested that the molten iron-silicate glasses (from inherent material) plays a more significant role than previously realized. Austin et al. (1984), for example, support this result by noting that when a coal was cleaned from 19.2% ash (2.26% S) to 9.3% ash (1.53% S) no change was noted in either the slagging propensity or the slag composition. In fact, they note that the slagging problem may have actually increased for the cleaned coal.

The above discussion illustrates the need to determine the dominant mechanism for

iron capture by silicates and to develop a modelling strategy to predict the amount of captured iron. By combining this iron capture mechanism with the extraneous pyrite oxidation mechanisms in the literature, it should be possible to determine the overall fate of iron during the combustion of pulverized coal.

Chapter 2

2. Experimental Apparatus and Procedures

One of the most important, and unique, aspects of this work was the use of a self-sustaining laboratory scale combustor to burn a number of well characterized coals. Fly ash samples from these experiments were then used to determine dominant ash formation mechanisms, and quantify the partitioning of iron during combustion (Chapter 4). The laboratory scale downfired combustor was equipped with a temperature measuring system, a gas analysis train, and a particle sampling system. Each experiment performed followed the same general procedure; heat the furnace to coal ignition temperatures, begin feeding coal, allow the furnace temperatures to stabilize, measure furnace temperature profiles, and collect particle samples. Gas concentration measurements were also taken to ensure the desired combustion environment was maintained in the furnace.

2.1 Laboratory Scale Combustor

The combustor used in this study, Figure 2.1.1 is described in several other references (Bassham, 1992, Bose, 1989, Gallagher, 1992, Scotto, 1989). The combustor, 20 feet long, was a 6" ID tube constructed from sections of formed Zircar refractory and insulated with several inches of Kaowool insulation. The inlet of the furnace is

Figure 2.1.1 Laboratory Scale Combustor

comprised of a cone cast from Kaocrete refractory. In addition, approximately the first 9 feet of the furnace are lined with cast silica carbide for durability. Sample ports, comprised of 2" mullite tubes, were placed along the length of the furnace for temperature measurements and gas or particle extraction. After run 68 it was necessary to rebuild the combustor due to the collapse of the upper section. In the rebuilt combustor the first 4 feet are constructed of cast Kaocrete of the same dimensions as the Zircar previously used. The kaocrete section was further lined with cast silica carbide for durability. The ports in the combustor section above the floor were formed by casting a block of refractory (Kaocrete or Kaolite) with the appropriate ports in place. In both designs the furnace outlet is an ash trap formed from stainless steel plates and zircar tubing (Gallagher, 1992). Ash is deposited in the ash trap as the flue gases negotiate a 180° turn to travel up a vertical tube connected to the exhaust.

Several safety features have been included in the furnace design to minimize the possibility of accidents and catastrophic failure (Bassham, 1992, Bose, 1989). Surrounding the furnace, for example, is an air tight exhaust shroud. Air is drawn through the shroud into the exhaust, taking with it any noxious exhaust gasses that may have leaked out of the furnace. Another safety feature is a UV flame detector. This detector is connected to all of the fuel inlet systems, the coal feeder and an electric valve on the natural gas feed. Should the flame extinguish, an alarm is sounded and the fuel automatically shut off. Finally, a cooling water grid is installed

on the inlet to the furnace to prevent premature heating of the coal and possible flashbacks in the natural gas line.

2.2 Fuel Feed System

The fuel feed system for this furnace was designed to feed coal and/or natural gas. Coal was fed into the furnace utilizing an Acrison Series 105 volumetric screwfeeder and an air transport line as shown in Figure 2.2.1. To prevent bridging and channeling in the of the coal feeder, a pair of pneumatically driven vibrators were attached to the feeder assembly. In addition, the coal was blown off the tip of the screw into the furnace by a metered stream of room temperature air. This method prevented coal from sticking to the screw and causing screw breakage. In addition, as the coal feedrate was extremely variable, it was controlled (by adjusting the screw speed) according to stoichiometry calculations and gas concentration measurements as discussed later.

Natural gas was also utilized in this furnace to heat the firetube so that the coal would ignite. A metered stream of gas was fed into the furnace through a pair of stainless steel tubes set in the plenum (Figure 2.2.2). This natural gas (and air) flowrate was increased slowly over a period of 2-3 hours to avoid thermal stress on the furnace. When the exhaust temperature was 400-500°C the gas was slowly turned off while the coal was turned on.

Figure 2.2.1. Coal Feeder

Figure 2.2.2 Plenum Section of Furnace

2.3 Air Feed System

The air feed system for this furnace (Figure 2.3.1) was comprised of three major parts; the primary (or preheat) air, the transport air, and the UV purge air. The sum of these three parts comprised the combustion air in the furnace. In each case air was compressed by a 25 hp Dayton Speedair compressor and filtered to remove oil and water before arriving at the appropriate section.

In the first part, the primary air, compressed air was passed through a regulator and a laminar flow meter. The metered flow was then passed through a 9 kW Chromalux electric air preheater where it was heated to the desired temperature (in many cases this was not used). From the preheater, the air passed through an insulated pipe to the mixing section above the plenum (Figure 2.3.2). In this section coal (and transport air) mixed with the primary air before entering the furnace. It was somewhat important to make sure that the primary air feedrate was sufficient to entrain all of the coal completely or some coal would deposit in the mixing section.

The second part of the air feed system was the coal transport air. As previously mentioned, the role of the transport air was to force the coal off the tip of the screw to prevent screw breakage. The air was metered with a small laminar flow meter similar to the primary air at rates of 7-80 slpm. However, in this case the air was passed directly to the coal feeder, bypassing the preheater. This air stream was never

Figure 2.3.1 Air Feed System

Figure 2.3.2 Coal-Air Mixing Section

heated to avoid heating the coal prematurely, which would cause it to adhere to the screw. It was very important to observe the furnace when turning on the transport air. If the transport air was too high it aspirated coal into the furnace as it passed the tip of the screw. This coal aspiration rate was uncontrollable, therefore any feedrate control lost.

The last major part of the air feed system was the UV purge air. This air was used to prevent soot and coal from obscuring the UV sensor (causing it to continually shut off the system). In this section, air was metered with a rotameter. The air entered the furnace through a connection to the protective tube containing the UV sensor.

2.4 Temperature Measuring System

The temperature profile in each experiment was controlled by the coal mass loading and air preheat. The furnace temperature profile was measured along the length of the furnace. A temperature probe, consisting of a type R thermocouple (1.6 mm 'twisted wire' bead) and a ½" OD ¼" ID 2 water cooled jacket, was inserted into the furnace at the desired ports. The thermocouple bead was extended from the tip of the probe so that it was in the center of the furnace. The uncorrected temperature could then read from a junction box on the upper region of the furnace. For most experiments, the temperatures at the bottom two ports (14 and 13) were measured first followed by the odd numbered ports in the pit section of the furnace (in decreasing order up to the level of the floor, port 5). On the upper level of the furnace the temperatures at all of the ports were measured

Errors in the uncorrected temperature measurements were often as much as 10°C, especially in the upper regions of the furnace. This was due to the effect of burning coal in the temperature probe. As burning coal particles pass the probe, the temperature measurement at the thermocouple box often fluctuated as much as ± 10 -15°C. The average value was estimated from the fluctuating values and recorded. In addition, the temperature measurements were not corrected to take into account radiation losses from the thermocouple.

2.5 Gas Sampling System

In order to monitor the combustion environment in the furnace, a gas sample was continuously withdrawn from the furnace with a gas probe. Flue gas was drawn through the probe (essentially a watercooled tube) and, in the earlier experiments, quenched with a water spray. It was then passed through a knock out system where the sample was cooled and the water and particles removed (Figure 2.5.1). This dry, particle free stream, was analyzed for CO, CO₂, NO, and O₂ utilizing an analytical train described by Gahni(1990), Linak (1985), and Mereb (1991). By tuning the coal feeder until the gas concentrations were those predicted from stoichiometry calculations (and assuming complete combustion), it was possible to control the coal feedrate. The measured species concentrations were then used to analyze the data for subsequent modelling. The NO measurements were further used to determine the dilution rate of the particle sampling system as described in the next section.

For experiments involving substoichiometric conditions, the coal feed was set by first running the furnace at SR=1.2 and following the procedure outlined above. The desired stoichiometric ratio was then achieved by decreasing the air feedrate. In addition, the CO/CO₂ ratio was calculated from the measured concentrations and compared with those from equilibrium calculations. The measured values were typically consistent with the equilibrium values for each stoichiometric ratio.

Figure 2.5.1 Gas Sampling System

2.6 Particle Sampling System

The particle sampling system, Figure 2.6.1, included an isokinetic probe, a Mark II Anderson Cascade Impactor, and the previously mentioned gas analysis system. It was described in detail by Gallagher (1992). Ash, drawn into the probe (Figure 2.6.2) as isokinetically as possible, was rapidly quenched to room temperature with dilution air. The dilution air served to quench the reactions, cool the sample, and prevent water condensation. In addition, the amount of ash laden flue gas drawn from the furnace was controlled by using dilution air to make up the difference between the 1 ACFM total flow required by the Mark II and the desired withdrawal rate. The quenched sample was then drawn through the impactor and size classified. The actual dilution ratio between the collected sample and the furnace could then be determined by comparing the furnace and sample NO concentrations.

The impactor configuration depended on the degree of separation desired for each analytical technique. For example, samples to be analyzed by Atomic Absorption (AA) or Energy Dispersive X-Ray (EDX) were collected with the full impactor (size classifications can be seen in Table 2.6.1). Samples to be analyzed by Computer Controlled Scanning Electron Microscopy (CCSEM) and Mössbauer were collected with the full impactor (earlier samples), with just 3 size classifications, or as a total filter (see Figure 2.6.3). In all cases the contents of the preseparator cup were added to the first plate (or the total filter) for analysis. For the non-EDX samples, the

Figure 2.6.1 Particle Sampling System

Figure 2.6.2 Particle Sampling Probe

Figure 2.6.3 Impactor Configurations

impaction substrates were either Flouropore filters (all runs up to run 64) or polyethylene disks (all runs after Run 64). In both cases the impaction substrates were covered with a thin film of PEG-600 (polyethylene glycol MW-600) to prevent particle reentrainment due to bounce off (Lodge, 1986). For the samples collected for EDX-Auger analysis silver membrane filters (2.5 cm) were placed on paper impaction substrates. These silver membrane filters were utilized to minimize charging effects when the collected particles were analyzed with an electron beam (Scotto, 1989). In all cases the after-filters were Flouropore 0.2 μm teflon filters.

Table 2.6.1 Cut Off Diameters for Mark II Impactor

Impactor Stage	Cut Off Diameter (μm)
Cup	>9.0
1	9.0
2	5.8
3	4.7
4	3.3
5	2.1
6	1.1
7	0.65
8	0.43
After Filter	<0.43

2.7 General Experimental Procedure

Although several types of experiments were performed to explore the effect of temperature, coal composition, and stoichiometric ratio on the partitioning of iron, all of the experiments followed the same general procedure. At the beginning of each experiment a number of calculations were performed to determine the necessary combustion air flow and resulting CO₂ concentration for a given coal feedrate and stoichiometric ratio. The furnace was then slowly heated with natural gas until the exhaust temperature reached 400-500°C. At this point, the air flowrate was set to the necessary value and the coal turned on. After the exhaust temperature stabilized such that it did not change more than $\pm 5^{\circ}\text{C}$ in $\frac{1}{2}$ hour, a temperature profile of the furnace was measured (as previously discussed). When the measured gas concentrations were stabilized after the temperature profile (approximately 10-15 minutes) the furnace gas composition was determined and noted on the strip charts for analysis after the experiment.

The particle samples were collected under each set of furnace conditions by inserting the particle probe (with the dilution air set at the previously determined value) and drawing the sample from the furnace. One experimenter noted the sampling time and the total gas volume sampled while another tracked the NO concentration from the particle probe and the CO₂ concentration in the furnace (to ensure that the coal feedrate did not change appreciably). After each sample was taken, the impactor

was disassembled , the samples removed, cleaned (if necessary), and reloaded. Before each sample was begun a blast of compressed air was directed down the sample line to clear any ash that had deposited.

When the desired set of particle samples were complete, the particle probe was removed and the furnace gas composition noted. If more samples were to be collected, the conditions were changed and the temperature again allowed to stabilize. At this point the process, beginning at the temperature profile, was repeated.

This experimental procedure was the result of several experiments (conducted with Neal Gallagher, 1992). In the initial experiments the procedure, and the particle sampling system, was much more complex. Subsequent experiments resulted in the refinement, and simplification, of the experimental procedure. For example, initially one experimenter was responsible for controlling the particle sampling rate, tracking the NO concentration, and preparing the next set of samples. After several experiments it was decided that one experimenter should be in control of the particle sampling system, including preparing the system before the experiment. The other experimenter was then responsible for calculating the necessary feedrates and controlling the furnace combustion conditions. This procedure resulted in increased efficiency during the experiments and was successful in achieving replicates both within an experiment and between separate experiments (Gallagher, 1992).

Chapter 3

3. Analytical Techniques and Coal Characterization

This work was performed as part of a larger effort, involving many diverse investigating groups, to elucidate mineral matter transformations during pulverized coal combustion. Due to the nature of this joint effort, a wide range of analytical techniques were available to characterize both the study coals and the collected fly ash. For example, investigators at the University of Kentucky performed CCSEM and Mössbauer analysis, among other techniques, on the study coals and selected ash samples. Auger, Atomic Absorption-Emission (AA), Energy Dispersive X-Ray (EDX), and X-Ray Diffraction (XRD) analysis were performed on selected ash samples by the author at the University of Arizona. Mössbauer analysis was also performed by the author, in conjunction with Dr. Roy Emrick, at the University of Arizona. Finally, Transmission Electron Microscopy (TEM) was performed by Dr. Roger Graham at Arizona State University.

The coals utilized in this study were chosen to represent a wide range of mineral matter composition, distribution, and coal types. A discussion on the selection process can be seen elsewhere (Boni et al., 1990). Basic information on the study coals, including ash composition, were provided by the Foster Wheeler Development Corp. More detailed analysis was then performed by the University of Kentucky

group to provide information on the original mineral matter. Specifically, the minerals present were identified and their size distributions estimated. Although the University of Kentucky group utilized many different techniques for this analysis (Boni et al., 1990), the techniques important for this study were Computer Controlled Scanning Electron Microscopy (CCSEM) and Mössbauer analysis.

3.1 Analytical Techniques

For this work the primary analytical tools included Atomic Absorption-Emission (AA), Computer Controlled Scanning Electron Microscopy (CCSEM), and Mössbauer. Other methods include Energy Dispersive X-Ray (EDX), and Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), and Auger Spectroscopy.

3.1.1 Atomic Absorption-Emission

One of the primary analytical techniques used to obtain composition data for this work was Atomic Absorption/Emission. Samples analyzed by atomic absorption were placed into a 55 ml polystyrene vial and dissolved by addition of 15 ml of dissolving acid (see Table 3.1.1.1 for compositions). After the sample was allowed to remain undisturbed for a few days, it was placed in an ultrasonic bath to expedite dissolution. When the sample had dissolved (typically 1-2 more days), 15 ml of boric

acid solution (see Table 3.1.1.1) was added and the sample sonicated again. The boric acid was added after the reactions involving fluorine (eg; silicate dissolution) were complete to capture excess fluorine ions (to protect the equipment) and to prevent silicon hexafluoride evaporation. The cesium (in the boric acid solution) was necessary to prevent loss of alkali species in the flame (Bassham, 1992).

Table 3.1.1.1 AA Analysis Solution Compositions

	Dissolving Acid (ml)	Acid Blank (ml)	Dilution Acid (ml)	Boric Acid (ml)
HCl (34%)	100	-	-	-
HNO ₃ (70%)	100	-	-	-
HF (49%)	300	-	-	-
DI Water	500	-	150	733
Cs Sol. (2000 ppm)	-	150	-	267
Dissolving Acid	-	200	200	-
Boric Acid	-	450 (25 g/l)	450 (25 g/l)	56.6 g (H ₃ BO ₃)

The sample was then analyzed for Fe, Si, Al, K, Na, Ca, and Mg utilizing a Perkin-Elmer 2830 Spectrophotometer and the standard procedure outlined by Perkin-Elmer. Standards for this analysis were obtained from VWR in 1000 ppm concentrations and diluted to the desired concentrations with a dilution acid solution to ensure that the standard contained the same background species as the sample

(boric acid, cesium, etc.). The measured concentrations (ppm) were then used to determine mass loadings in each size range, species and mass distributions, and the total ash composition as compared to the original coal analysis.

3.1.2 Mössbauer

Probably the most important analytical tool used in this work was Mössbauer analysis, performed both by the University of Kentucky and by the author (in conjunction with Dr. Roy Emrick) at the University of Arizona. In this technique the sample (from the impactor stage 1 and the cup, or the total filter) was mounted in a thin "window" type sample holder (approximately 1" in diameter). Gamma radiation was then passed through the sample and the amount absorbed measured as a function of the source speed (or gamma beam energy). The chemical state of the iron was then determined by locating the characteristic absorption peaks for each compound. For example, the glass was typically designated as a doublet near the center of the spectrum. Oxide forms also had characteristic 'signature' sets (Section 4.4). The fraction of iron in each state was then determined by fitting the area under all the curves.

This technique is very useful in exploring the chemical state of iron. However, it is limited primarily to iron, and therefore can not be used to distinguish other compounds (quartz or kaolinite, for example). In addition, as a relatively large

sample is needed for this analysis, only the iron distribution in the ash as a whole could be determined (no size classified information could be obtained).

3.1.3 Computer Controlled Scanning Electron Microscopy (CCSEM)

This technique, described in detail elsewhere (Boni et al., 1990), was performed at primarily at the University of Kentucky with some later samples analyzed at the University of North Dakota Energy Research Center (UNDERC). Coal samples were mounted in an epoxy, cross-sectioned, and polished. Ash samples were mounted on a filter for analysis. A computer controlled SEM utilized the backscattered electron intensity and a decreasing grid routine to determine the location and size of mineral particles. After determining the particle size, the beam was focussed on the center of the particle and an EDX spectrum (discussed later) collected. The resulting data files were then analyzed, by the University of Kentucky, to group the individual particles into the appropriate mineral or mixed category.

Although this technique provided interesting size and composition information on ash and original mineral particles, care must be taken in interpreting the results. For example, CCSEM may determine that a particle contains Fe, Si, Al, and Ca. This does not indicate that the particle is a single ash particle containing all of these elements. Instead, the particle may be an agglomerate of several smaller particles of different composition (Section 4.6). This is also the case with the original mineral

matter. A particle designated as kaolinite by CCSEM, for example, may contain appreciable amounts of impurities. In general the information given by this technique, when interpreted carefully, can provide interesting information on the ash behavior during combustion (Section 4.4).

3.1.4 Transmission Electron Microscopy (TEM)

Another important analytical tool used in this work was Transmission Electron Microscopy (TEM). This analysis, described in detail in Chapter 4, was performed on ash from the Beulah Lignite and Illinois #6 coals by Dr. Roger Graham at the Center for High Resolution Electron Microscopy (CHREM), Arizona State University. In this technique, a small amount of ash from the ashtrap is pulverized into thin sections and placed on a copper grid. A high power electron beam is then passed through the sample. As the beam electrons pass through the sample, they may interact with the sample to form x-rays or Auger electrons (as discussed in subsequent sections) or they may be scattered by the crystalline lattice itself. By focussing on a particle in the thin section, it is possible to determine both particle composition (x-ray methods) and crystallographic information (electron diffraction methods). In addition, this technique has an extremely high resolution (approximately 20Å), allowing analysis of very small particles.

This technique is uniquely suited to exploring the composition and physical state of

very small particles. However, because the particles must be very small for analysis by this technique, some important morphology information may be missed. For example, this technique (Section 4.6) found pieces of material identified as an iron oxide crystal. This technique, unfortunately, could not reveal the original form of this crystalline particle (eg; agglomerated with other particles or isolated).

3.1.5 Energy Dispersive X-Ray (EDX)

The Energy Dispersive X-Ray (EDX) technique utilizes an electron beam to determine elemental composition of the sample. When beam electrons interact with the sample, they may collide with electrons in the atom's inner electron shells. When this occurs, the inner electron is ejected from the shell. An outer shell electron can then release energy, the form of an x-ray, and fall into the inner shell. The atom can also absorb the energy change and eject an outer shell electron (Auger electron formation). Since the energy bandwidths are element specific, the resultant x-rays (or auger electrons) may be measured and the sample composition determined.

This technique was utilized to determine the morphology and composition of collected fly ash samples as described in Chapter 4. A small section (approximately 5mm x 5mm) of a particle laden silver membrane filter was mounted on a SEM mount and carbon coated (to minimize charging). These samples were then analyzed in a JEOL Scanning Electron Microprobe. For the ash analysis via EDX mapping,

an agglomeration was initially identified at relatively low magnification, imaged (SEM) and mapped for Fe, Si, Al, K, Na, Ca, Mg and Au by EDX. The Si and Fe maps of the agglomeration were then used to 'pinpoint' any iron particles in contact with silicate particles. The magnification was then increased and the process repeated until the iron particles were determined to be physically agglomerated with silicate particles (see Section 4.5).

3.1.6 X-Ray Diffraction (XRD)

The next major analytical technique utilized to characterize the original coal and, to a lesser extent, the ash was X-Ray Diffraction. In this technique a sample is bombarded with an x-ray beam at various angles. When the x-ray beam is aligned with a crystallographic plane, the beam is diffracted according to Bragg's law. By determining the angle of diffraction, and utilizing Bragg's law, it is possible to determine the lattice spacings (and therefore, often, the identity) of the crystals in the lattice. This technique was utilized to determine the crystalline mineral matter present in the parent coals, and to determine the presence of iron oxide crystals in the collected ash (see Section 4.5).

3.1.7 Auger

The last analytical technique, utilized to a small extent, was Auger analysis which was

performed on selected ash samples (see Chapter 4). A small piece of a particle laden silver membrane filter was analyzed with a Perkin Elmer Scanning Auger Microprobe. As an electron beam bombards a surface, electrons, called Auger electrons, are formed from beam-sample interactions (see Section 3.1.5). These ejected electrons may escape the sample, and be analyzed, but only if they are close to the surface. Due to this spacial limitation (only a few atomic layers) this is primarily a surface analysis. In addition, as each element has a characteristic 'fingerprint' of emitted Auger electron energies, it is possible to determine qualitatively (and semi-quantitatively) the elemental species on the surface of the sample by determining the number of electrons in a given energy range .

3.2 Coal Characterization

The suite of coals selected for this work were carefully analyzed by a number of techniques and investigators to fully characterize both the coal and its original mineral matter. Basic coal information, including the proximate and ultimate analysis and the ash composition, was determined by the Foster Wheeler Development Corporation. Information on the mineral matter composition and size distribution was determined by CCSEM and Mössbauer analysis at the University of Kentucky.

3.2.1 Coal Analysis (Foster Wheeler Development Corp.)

The basic coal information provided by the Foster Wheeler Corporation can be seen in Table 3.2.1.1 (Wet Basis) and Table 3.2.1.2 (Dry Basis). There are several interesting points to note about this selection of coals. First it is interesting to note the range of ash content in the study coals (dry basis), 6.44% in the Subbituminous Eagle Butte to 23.35% in the Bituminous Upper Freeport coal. The Eagle Butte was found to contain a large amount of calcium as compared to the other study coals. Three of the Bituminous coals in this study, the Kentucky No. 9, the Kentucky No. 11, and the Illinois No. 6 contained a large amount of iron in the ash. The Upper Freeport coal, on the other hand, contained largely silicon and aluminum.

Table 3.2.1.1 Coal Analysis from Foster Wheeler Development Corp. (Wet Basis)

	Upper Freeport	Beulah Lignite	Eagle Butte	Kentucky No. 11	Kentucky No. 9	Illinois No. 6
Prox. Anal. (wt%)						
Fixed C	52.27	30.91	36.22	41.96	42.86	42.15
Vol.Mat.	23.99	29.28	33.76	33.24	34.49	35.92
Ash	23.23	9.65	4.82	20.96	14.33	8.62
Moisture	0.51	30.16	25.20	3.94	8.32	13.31
Ult. Anal. (wt%)						
Carbon	64.57	41.30	50.26	57.75	59.98	59.87
Hydrogen	4.07	2.92	3.77	4.42	4.27	4.55
Oxygen	3.92	13.84	14.60	7.64	7.92	8.52
Nitrogen	1.63	0.82	1.01	1.29	1.63	1.37
Sulfur	2.07	1.31	0.34	4.22	3.55	3.76
Ash	23.23	9.65	4.82	20.96	14.33	8.62
Moisture	0.51	30.16	25.20	3.94	8.32	13.31
H.H.V., Btu/lb	11395	6942	8733	-	10793	10693
Sulfate S (wt%)	0.00	0.00	0.00	0.00	0.00	0.00
Pyrite S (wt%)	1.41	1.07	0.06	2.55	1.62	1.11
Organic S (wt%)	0.66	1.24	0.28	1.67	1.94	2.62
Soluble Alkalies (ppm)						
Na	320/400	7500/7250	820/820	366/376	550/500	2177/2339
K	2300/2400	150/170	80/110	3519/3377	2500/2600	2381/2378
Ca	3700/3700	14125/13875	7000/8250	4926/4824	2900/2950	5792/5829
Mg	1200/1200	3375/3250	1860/1890	985/1032	850/850	1769/1762

From Foster Wheeler Development Corporation (Boni et al., 1990)

Table 3.2.1.2 Coal Analysis from Foster Wheeler Development Corp. (Dry Basis)

	Upper Freeport	Beulah Lignite	Eagle Butte	Kentucky No. 11	Kentucky No. 9	Illinois No. 6
Prox. Anal. (wt%)						
Fixed Carbon	52.54	44.27	48.43	43.65	46.75	48.63
Vol. Mat.	24.11	41.92	45.13	34.56	37.62	41.43
Ash	23.35	13.81	6.44	21.79	15.63	9.94
Ult. Anal. (wt%)						
Carbon	64.90	59.13	67.20	60.10	65.42	69.05
Hydrogen	4.09	4.18	5.04	4.60	4.66	2.25
Oxygen	3.94	19.82	19.51	7.90	8.63	9.83
Nitrogen	1.64	1.18	1.35	1.20	1.78	1.58
Sulfur	2.08	1.88	0.46	4.40	3.88	4.34
Ash	23.25	13.81	6.44	21.80	15.63	9.94
H.H.V., Btu/lb	11453	9940	11675	10430	11773	12335
Sulfate S (wt%)	0.00	0.00	0.00	0.00	0.00	0.00
Pyrite S (wt%)	1.42	1.10	0.07	2.65	1.77	1.28
Organic S (wt%)	0.66	1.78	0.39	1.74	2.11	3.06
Soluble Alkalies (ppm)						
Na	320/400	7500/7250	820/820	366/376	550/500	2177/2339
K	2300/2400	150/170	80/110	3519/3377	2500/2600	2381/2378
Ca	3700/3700	14125/13875	7000/8250	4926/4824	2900/2950	5792/5829
Mg	1200/1200	3375/3250	1860/1890	985/1032	850/850	1769/1762

From Foster Wheeler Development Corporation (Boni et al., 1990)

Table 3.2.1.3 Ash Analysis from Foster Wheeler Development Corp.

	Upper Freeport	Beulah Lignite	Eagle Butte	Kentucky No. 11	Kentucky No. 9	Illinois No. 6
% Ash (Dry, wt%)	23.35	13.81	6.44	21.79	15.63	9.94
% S (wt%)	2.07	1.88	0.34	4.48	3.88	4.34
Chemistry (wt%)						
SiO ₂	50.6	21.6	28.4	46.7	44.6	46.1
Al ₂ O ₃	24.6	14.5	15.5	19.4	20.6	18.0
TiO ₂	1.2	0.0	0.9	0.9	1.1	0.9
Fe ₂ O ₃	13.5	12.2	6.1	20.0	22.4	20.5
CaO	2.2	17.1	26.4	4.4	3.1	5.3
MgO	1.4	4.2	6.2	0.9	1.1	0.6
Na ₂ O	0.3	6.1	2.0	0.3	0.9	1.3
K ₂ O	3.1	0.3	0.2	2.2	2.6	2.1
SO ₃	2.4	21.1	13.7	5.0	4.7	4.4
P ₂ O ₅	0.1	Nil	0.7	0.2	0.1	0.1
Ash Fusion Temps. (°F)						
<u>Reducing</u>						
Init. Def	2178	2241	1996	2293	2203	2261
Soft Temp. (Sph.)	2255	2266	2108	2300	2394	2300
Soft Temp. (Hem.)	2320	2272	2149	2332	2420	2315
Fluid Temp.	2369	2274	2163	2353	2435	2460
<u>Oxidizing</u>						
Init. Def	2410	2168	2251	2299	2231	2220
Soft Temp. (Sph.)	2496	2208	2308	2334	2405	2261
Soft Temp. (Hem.)	2518	2217	2358	2366	2436	2330
Fluid Temp.	2535	2219	2358	2379	2457	2495

Foster Wheeler Development Corp. (Boni et al., 1990)

Finally, the Beulah Lignite coal contained a great deal of sodium and an appreciable amount of calcium, as compared to the other coals.

3.2.2 Mineral Matter Composition

In order to fully model and understand the mineral matter transformations that occur during combustion, it was necessary to determine what mineral species are present in the original coal. The University of Kentucky group utilized CCSEM analysis of the coals to determine the mineral constituents. Table 3.2.2.1 shows the mineral matter present in the various coals. As this work is focussed primarily on the fate of iron and its interactions with silicates, it is important to know both the initial form of the iron and the types of silicates present in the coal.

It is important to note that most of the study coals contain iron predominantly as pyrite (98-100%). The only exception to this trend was the Upper Freeport. In this coal only 79% of the iron is as pyrite, with the balance being distributed throughout other species (see Table 3.2.2.2). For this work the iron as Fe^{2+} in clays was assumed to react to form glass. The other compounds, siderite (FeCO_3) and jarosite ($\text{K}_2\text{SO}_4 \cdot x\text{Fe}_2(\text{SO}_4)_3$) were assumed to behave as pyrite.

Another important parameter to note is the distribution of the silicate species and the average composition of the various silicate species. In the bituminous coals most

of the silicates are as quartz (SiO_2), Illite $((\text{FeO}, \text{CaO}) \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O})$, and "mixed silicates" (composition varies). In the other two study coals quartz and "mixed silicates" are also important. However, illite is replaced by kaolinite $(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O})$ in these coals. As seen from Tables 3.2.2.3 through 3.2.2.8, the silicate species in these coals contain appreciable amounts of impurities (note CCSEM does not measure H, O, or C) as compared to the previously stated 'pure' compositions. The presence of these impurities would serve to depress the melting point of the solid mixture, allowing the these species to melt at a lower temperature than the 'pure' species.

Another important parameter for this study is the relative amounts of extraneous and inherent mineral matter. By assuming that the inherent mineral matter agglomerates as the char burns away, it is possible to estimate the extraneous fraction of the original mineral matter (see Chapter 4). Table 3.2.2.9 shows the relative fraction of inherent mineral matter in the coal. The ratio of silicates to iron in the inherent ash, also seen in Table 3.2.2.9, is also a very important parameter in determining the behavior of iron during combustion. The amount of silicates, relative to the iron, would be expected to be significant in the partitioning of iron between the glassy (silicate captured) phase and iron oxide.

Table 3.2.2.1 Discrete Mineral Matter, from CCSEM, in Study Coals

Mineral (wt %)	Beulah Lignite	Eagle Butte	Kentucky No. 9	Kentucky No. 11	Upper Freeport	Illinois No. 6
Quartz	12	40	12	19	10	20
Kaolinite	30	13	6	8	7	6
Illite	1	2	23	16	35	10
Chlorite	-	-	-	-	1	<1
Montmorillonite	1	2	<1	1	1	<1
Mixed Silicates	13	16	34	23	19	18
Pyrite	26	4	16	24	18	28
Jarosite	3	-	-	-	<1	-
Fe ²⁺ Sulfates	2	<1	<1	<1	-	2
Gypsum	-	-	-	1	-	1
Fe-rich minerals	<1	4	-	<1	1	1
Ca-rich minerals	1	3	3	4	2	7
Ti-rich minerals	-	1	<1	-	<1	-
Apatite	-	-	-	-	-	-
Misc. Mixed	10	15*	5	3	6	7

From University of Kentucky

* Includes significant (2 to 3 wt%) Ca-Sr(Si)-Al-P mineral-crandallite?

Table 3.2.2.2 Iron Distribution, from Mössbauer, in Study Coals

% Iron in	Beulah Lignite	Eagle Butte	Kentucky No. 9	Kentucky No. 11	Upper Freeport	Illinois No. 6
Pyrite	100	100*	97	98	79	>99
Siderite	-	-	-	-	7	-
Fe ²⁺ in Clays	-	-	3	2	11	-
Jarosite	-	-	-	-	3	-
Fe ²⁺ Sulfates	-	-	-	-	-	<1
Wt% Pyritic Sulfur	0.60	<0.07	2.33	3.92	1.42	1.48

From University of Kentucky

* Absorption very weak, could include some oxyhydride and/or jarosite

Table 3.2.2.3 Mineral Species Composition: Beulah Lignite

Mineral Species	Elemental Composition										
	Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz				97	1				1	1	
Kaolinite			42	52	2	1		1	1	1	1
Illite	1		34	50	1			8	2	1	3
Montmorillonite			20	60	4	1		2	5		1
Misc. Silicates			30	57	3	1		2	3	2	2
Jarosite			3	6	39			8	3	3	39
Pyrite		1		1	66					2	31
Fe-rich (siderite)		3	4	8	3	2	1	2	4	2	69
Ca-rich (maceral)		3	3	3	13	1	1		71	1	4
Sil/Sul*	1	1	26	39	14	1		4	9	2	2
Sil/Pyr*			32	22	17	7		10	1		10
Misc. Mixed	2	4	12	15	24	4	2	3	20	15	6

Table 3.2.2.4 Mineral Species Composition: Illinois No. 6

Mineral Species	Elemental Composition										
	Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz				96	1			1		1	1
Kaolinite			41	51	4	1		1		1	1
Illite			28	50	5			13	1	1	2
Chlorite		5	21	36	2			1			35
Montmorillonite	2		16	72	5			1	2	1	1
Misc. Silicates		1	21	61	2			10	2	2	4
Fe ²⁺ Sulfate			1	2	48				1	1	46
Pyrite			1	1	65						32
Fe-rich (siderite)			1	4	9						82
Ca-rich (calcite)			1	1	2		1	1	91		
Ti-rich (rutile)			3	4	7	1				82	
Apatite (Ca, P)			1	1			28	1	66	2	1
Sil/Sul*	1	1	15	43	23	1		7		2	7
Sil/Pyr*			14	48	18	1		8	1	2	10
Misc. Mixed	1	3	13	30	12	8	2	9	7	10	10

Table 3.2.2.5 Mineral Species Composition: Kentucky No. 9

Mineral Species	Elemental Composition (mole %)										
	Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz			3	93	1			1		1	2
Kaolinite			42	51	3	1		2	1	1	1
Illite	1		28	52	4	1		11	2	1	4
Montmorillonite	1		19	72	3			2	1	1	
Misc. Silicates			18	63	3	1		9	2	2	5
Fe ²⁺ Sulfate			2	2	53					1	41
Pyrite			2	2	61					1	34
Ca-rich (calcite)		1	1	2	3	1	1	1	88	1	1
Ti-rich (rutile)		1	6	10	3				1	77	2
Sil/Sul*			17	42	28			6	3	2	3
Sil/Pyr*			15	36	24			6	2	1	14
Misc. Mixed	1	2	14	21	14	10	4	4	14	6	11

Table 3.2.2.6 Mineral Species Composition: Eagle Butte

Mineral Species	Elemental Composition (mole %)										
	Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz			1	96				1	1	1	1
Kaolinite	1		41	52	1	1		1	2	2	1
Illite			28	53	1	2		10	3	2	2
Montmorillonite			18	68	2			2	4	4	1
Misc. Silicates	1	2	20	50	2	2		3	6	2	4
Fe ²⁺ Sulfate			1	2	55				1	1	40
Pyrite		1	60				2		36		
Fe-rich (siderite)			1	3	2		2	1	4	2	85
Ca-rich (calcite)	1		1	3	4	1	1	3	84	1	5
Ti-rich (rutile)		1		5	2	1		1	2	87	1
Sil/Sul*	1		25	50	8	3		1	9	4	0
Sil/Pyr*			14	56	4			5	14	3	2
Misc. Mixed*	1	2	22	15	8	4	11	4	28	8	4

*includes significant amount (up to 5 wt%) of Ca-Sr(Si)-Al-P mineral, possibly crandallite

Table 3.2.2.7 Mineral Species Composition: Kentucky No. 11

Mineral Species	Elemental Composition (mole %)										
	Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz			3	94				1		1	
Kaolinite			40	51	3			2	2	2	2
Illite			28	54	3			10	1	2	4
Chlorite			27	35	3			1			31
Montmorillonite	2		17	73	2	1		3	1	2	1
Misc. Silicates			21	61	2			11	2	2	4
Gypsum			2	4	50			1	42	1	1
Fe ²⁺ Sulfate			1	5	42			1		2	48
Pyrite			2	3	63			1		1	33
Fe-rich (siderite)	1		6	13	9			1	1	1	69
Ca-rich (calcite)	1	1		1	2				89		1
Ti-rich (rutile)		1	6	10	3				1	77	2
Sil/Sul*			18	40	27	2		8	2	1	5
Sil/Pyr*			14	41	20			7	4	1	12
Misc. Mixed			11	30	11	4	3	6	14	17	6

Table 3.2.2.8 Mineral Species Composition: Upper Freeport

Mineral Species	Elemental Composition (mole %)										
	Na	Mg	Al	Si	S	Cl	P	K	Ca	Ti	Fe
Quartz			2	93				1	1	1	1
Kaolinite	1	1	38	49	2	3		2	2	1	1
Illite	1	1	28	51	1	2		12	2	2	3
Chlorite	2	4	21	36	2	1		1	2	1	31
Montmorillonite	20	71	2	1		2	1		2		
Misc. Silicates	1	1	20	57	2	1		7	1	2	10
Jarosite		1	6	11	44			6	1	3	26
Pyrite		1	2	4	59				1	1	33
Fe-rich (siderite)		3	4	8	3	2	1	2	4	2	69
Ca-rich (calcite)		1	4	4	2			1	84	1	2
Ti-rich (rutile)	1	1	3	9	1			1		82	3
Sil/Sul*	1	1	24	46	14	4		2	4	2	10
Sil/Pyr*			6	12	43			2	17	2	10
Misc. Mixed	1	3	13	30	12	8	2	9	7	10	10

Table 3.2.2.9 Fraction Inherent Mineral Matter (from CCSEM) for Study Coals

Coal	MF Inherent		Inh Sil/ tot Pyrite
	Pyrite	Silicate	
Kentucky No. 9	0.65	0.77	4.03
Illinois No. 6	0.57	0.63	1.49
Kentucky No. 11	0.69	0.81	2.41
Beulah Lignite	0.58	0.86	2.40
Upper Freeport	0.84	0.77	3.50
Eagle Butte	0.75	0.82	19.42

3.2.3 Mineral Matter Size

The size distribution of the original mineral matter was determined as part of the previously described CCSEM analysis of the coals. The results can be seen in Tables 3.2.3.1 through 3.2.3.6. In addition, the fraction inherent mineral matter was also used to estimate a mean pyrite and silicate size for the inherent material. It was assumed that the small particles were more likely to be included in the carbon matrix. The mass mean size, Table 3.2.3.7, was then determined from the mass fraction in each size range (starting at the smallest) and the total mass fraction of inherent material.

It can be seen from these tables that in the Beulah Lignite coal the pyrite was primarily in the large size range. The quartz particles were more evenly dispersed, while the remaining silicates were primarily in the small sizes. In the Upper Freeport coal the pyrite was primarily in the large size ranges ($>40\ \mu\text{m}$ diameter) while the silicates were more evenly dispersed. Pyrite in the Kentucky coals was fairly evenly distributed through all the measured size ranges. Most of the silicates in the Kentucky #9 were in the small size ranges. Silicates in the Kentucky 11 were a little more evenly distributed, but most of the mass was still less than $20\ \mu\text{m}$. Pyrite in the Illinois #6 was primarily in the $10\text{-}40\ \mu\text{m}$ range. The silicate material was also primarily less than $20\ \mu\text{m}$.

Table 3.2.3.1 Mineral Size Distribution (μm) for Beulah Lignite

Mineral	<2.5 (Wt%)	2.5-5 (Wt%)	5-10 (Wt%)	10-20 (Wt%)	20-40 (Wt%)	>40 (Wt%)
Quartz	11	11	17	23	19	18
Kaolin.	42	7	9	13	12	17
Montmor.	--	--	--	--	--	--
Mix. Sil.	73	6	7	7	7	0
Pyrite	1	1	3	12	26	56
Total	27	7	8	13	16	30

From the University of Kentucky

Table 3.2.3.2 Mineral Size Distribution (μm) for Illinois No.6

Mineral	<2.5 (Wt%)	2.5-5 (Wt%)	5-10 (Wt%)	10-20 (Wt%)	20-40 (Wt%)	>40 (Wt%)
Quartz	20	27	24	22	5	1
Kaolin.	29	29	18	21	4	0
Montmor.	35	29	21	11	4	0
Mix. Sil.	30	27	19	14	5	4
Pyrite	8	6	10	33	29	13
Calcite	8	6	7	25	21	32
Total	22	17	15	23	15	8

From the University of Kentucky

Table 3.2.3.3 Mineral Size Distribution (μm) for Kentucky No.9

Mineral	<2.5 (Wt%)	2.5-5 (Wt%)	5-10 (Wt%)	10-20 (Wt%)	20-40 (Wt%)	>40 (Wt%)
Quartz	13	31	25	24	7	1
Kaolin.	20	35	24	14	6	1
Illite	26	24	17	14	8	11
Mix. Sil.	35	18	12	10	9	15
Pyrite	7	18	18	19	18	21
Total	24	21	17	15	11	12

From the University of Kentucky

Table 3.2.3.4 Mineral Size Distribution (μm) for Eagle Butte

Mineral	<2.5 (Wt%)	2.5-5 (Wt%)	5-10 (Wt%)	10-20 (Wt%)	20-40 (Wt%)	>40 (Wt%)
Quartz	21	10	20	17	20	12
Kaolin.	9	10	31	17	22	11
Illite	-	-	-	-	-	-
Mix. Sil.	37	16	18	8	5	16
Pyrite	9	7	22	30	28	3
Total	100	23	21	15	16	15

From the University of Kentucky

Table 3.2.3.5 Mineral Size Distribution (μm) for Kentucky No.11

Mineral	<2.5 (Wt%)	2.5-5 (Wt%)	5-10 (Wt%)	10-20 (Wt%)	20-40 (Wt%)	>40 (Wt%)
Quartz	19	25	23	16	12	5
Kaolin.	33	16	28	12	6	4
Montmor.	34	24	21	8	9	4
Mix. Sil.	26	14	20	15	14	11
Pyrite	10	9	14	14	21	33
Total	24	15	18	13	15	16

From University of Kentucky

Table 3.2.3.6 Mineral Size Distribution (μm) for Upper Freeport

Mineral	<2.5 (Wt%)	2.5-5 (Wt%)	5-10 (Wt%)	10-20 (Wt%)	20-40 (Wt%)	>40 (Wt%)
Quartz	8	14	26	20	26	6
Kaolin.	15	9	15	25	19	16
Montmor.	10	10	13	11	12	44
Mix. Sil.	12	16	15	21	12	23
Pyrite	4	2	13	13	14	54
Total	9	10	15	15	14	36

From the University of Kentucky

Table 3.2.3.7 Mass Mean Size of Inherent Material
(From Fraction Inherent Mineral Matter)

Coal	Silicates (μm)	Pyrite (μm)
Illinois No. 6	3.42	11.04
Kentucky No. 11	6.20	17.48
Kentucky No. 9	5.93	7.77
Upper Freeport	17.41	31.58
Beulah Lignite	7.43	31.07
Eagle Butte	7.63	13.02

Chapter 4

4. Experimental Results and Iron Behavior

In the course of this study many experiments were performed to collect data on mechanisms governing the formation of fly ash during combustion. Table 4.1 shows a general outline of the goals of these experiments. Figure 4.1 shows the time-temperature histories for these experiments. The initial experiments, performed in conjunction with Neal Gallagher (1992), yielded fly ash samples from a number of different coals and temperature profiles. Data from some of these 'burns' was used to determine the dominant mechanisms (eg; agglomeration) for iron and ash formation.

When these preliminary experiments were complete, the focus of this study narrowed to the partitioning of iron during combustion. Experiments were then performed to obtain base case iron partitioning data for the study coals. This data was used to explore the effect of coal type on iron partitioning. Other potentially important variables, temperature and stoichiometric ratio, were explored in the final set of burns.

The fly ash samples collected during the course of these experiments were initially analyzed by a number of techniques (described in Chapter 3) including Atomic

Absorption, CCSEM, and Mössbauer. From the AA results (ash), and the CCSEM analysis (coal), it was possible to determine the overall behavior of the ash and the iron during combustion. Finally, some interesting discrepancies were noted between the CCSEM and Mössbauer results for iron, therefore a number of additional techniques were utilized to determine the iron-silicate association in the ash.

Table 4.1 General Description of Experiments

Purpose	Run	Coal	Primary Analysis
Determine Overall Ash Behavior Under "Base" conditions	13-14	Beulah Lignite	Atomic Absorption Spectroscopy (AA)
	15-16	Eagle Butte	
	17-18	Kentucky #9	
	19-20	Illinois #6	
	21	Illinois #6	Atomic Absorption Spectroscopy (AA), CCSEM, Mössbauer
	22	Beulah Lignite	
	23	Eagle Butte	
	24	Kentucky #9	
	27-28	Kentucky #11	
	32-35	Upper Freeport	
Determine Effect of Temperature on Ash Behavior	36	Kentucky #9	Atomic Absorption Spectroscopy (AA), Mössbauer
	37	Kentucky #11	
	38	Beulah Lignite	
	40	Eagle Butte	
	47	Illinois #6	
	48	Beulah Lignite	
	56	Kentucky #11	

Table 4.1 General Description of Experiments (cont'd)

Purpose	Run	Coal	Primary Analysis
Determine Effect of Stoichiometric Ratio	57	Kentucky #11	Mössbauer
	58	Kentucky #11	
Determine Ash Behavior Under "Base" Conditions	59-60	K9/EB Blend	AA Spectroscopy
	61-64	Eagle Butte	Mössbauer
	65-69	Kentucky #9	
	70	Illinois #6	
	71	Upper Freeport	
Determine Effect of Temperature and Stoichiometric Ratio	72-74	Kentucky #11	
	75	Beulah Lignite	Mössbauer

Figure 4.1 Time Temperature Histories for Partitioning Experiments

4.1 Summary of Experiments and Experimental Conditions

The first set of experiments in this project were performed to obtain basic data on the ash formation mechanisms for several of the study coals. These experiments, Runs 13 through 20 (Table 4.1.1), yielded data on ash mass and composition versus size for the Beulah Lignite, Eagle Butte, Kentucky #9, and Illinois #6 coals. This information was then used to determine the dominant ash formation mechanisms for both the original mineral matter and the original iron. In a related study, by Neal Gallagher (1992), these and some subsequent experiments were discussed in more detail.

The next set of experiments, Runs 21 through 24, were performed to collect fly ash samples for CCSEM/Mössbauer analysis from the previously burned coals. Experimental parameters for these experiments can be seen in Table 4.1.1. Figures 4.1.1 through 4.1.4, show that the temperature profiles for this set were fairly similar. Peak temperatures were generally between 1300 and 1400 K and occurred between ports 2 and 3 of the combustor. The subsequent experiments of that set, Runs 27 through 35, yielded both basic ash information (from AA analysis) and samples for analysis by CCSEM/Mössbauer for the remaining study coals, the Kentucky #11 and the Upper Freeport. Of these burns, Runs 27, 32, and 35 are of particular importance in the iron partitioning study. Temperature profiles for these burns can

Table 4.1.1 Tabulation of Samples and Experiments

Run ID	Coal Name	Stoich. Ratio	Peak Gas Temp. (K)	Coal Feed (kg/h)	Samples		
					AA	Möss.*	Auger
13	Beulah Lignite	1.38	1601	2.3	A-D		
14		1.43	1596	2.2	A-D		E
15	Eagle Butte	1.32	1745	3.0	B-D		A
16		1.26	1684	2.3	A-D		E
17	Kentucky #9	1.26	1711	1.8	A-D		E
18		1.23	1746	1.8	A-D		E
19	Illinois #6	1.21	1665	1.8	A-D		E
20		1.26	1632	1.7	A-D, F		E
21		1.27	1635	1.7		A	
22	Beulah Lignite	1.32	1567	2.4		A	
23	Eagle Butte	1.26	1493	2.3		A	
24	Kentucky #9	1.22	1684	1.9		A	
27	Kentucky #11	1.25	1593	1.7	A-D	E	"Auger"
28		1.19	1613	1.8	A-D		E

* Includes CCSEM samples for Runs 21-35

Table 4.1.1 Tabulation of Samples and Experiments (cont'd)

Run ID	Coal Name	Stoich. Ratio	Peak Gas Temp. (K)	Coal Feed (kg/h)	Samples		
					AA	Möss.*	Auger
32	Upper Freeport	1.23	1620	1.7	A-E		E
33		1.24	1573	1.7	A-D		E
34		1.22	1573	1.8	A-D		E
35		1.22	1573	1.7	A-D		"Auger"
36	Kentucky #9	1.28	1646	1.9	A		
		1.30	1439	1.0	B-C		
37	Kentucky #11	1.26	1534	2.0	A		
		1.28	1378	0.44	B-C		
38	Beulah Lignite	1.28	1558	2.9	A		
		1.26	1405	1.2	B-C		
40	Eagle Butte	1.24	1633	3.2	A	B	
		1.23	1508	1.1	C,D		
47	Illinois #6	1.30	1577	1.3	A,C	B,D	
		1.24	1641	2.3	E,G	F,H	

* Includes CCSEM samples for Runs 21-35

Table 4.1.1 Tabulation of Samples and Experiments (cont'd)

Run ID	Coal Name	Stoich. Ratio	Peak Gas Temp. (K)	Coal Feed (kg/h)	Samples		
					AA	Möss.*	Auger
48	Beulah Lignite	1.26	1463	1.6	A,C	B,D	
		1.37	1518	2.6	E	F	
56	Kentucky #11	1.25	1513	1.3	B	A,C	
		1.20	1702	2.1	E	D,F	
57	Kentucky #11	0.80	1390	1.8			
58		1.32	1713	1.8			
59	K9/EB Blend	1.35	1456	1.8	A-D		
60		1.35	1484	1.8	A-D		
61	Eagle Butte	1.33	1466	2.1		B	
62		?	1513	?		A	
63		?	1580	?		A-C	
64		1.33	1604	2.3	B	A	
65	Kentucky #9	?	188	?	A	B	
66		1.31	1499	1.7	B	A,C	
67		1.30	1539	1.7	B	A,C	

* Includes CCSEM samples for Runs 21-35

Table 4.1.1 Tabulation of Samples and Experiments (cont'd)

Run ID	Coal Name	Stoich. Ratio	Peak Gas Temp. (K)	Coal Feed (kg/h)	Samples		
					AA	Möss. *	Auger
68	Kentucky #9	1.20	1475	2.3	B	A	
69		1.21	1633	3.2		A-D	
70	Illinois #6	1.19	1718	3.5	A	B,C	
71	Upper Freeport	1.19	1684	3.6	B	A,C	
72	Kentucky #11	0.72	1693	2.8		A,B	
73		0.8	1574	2.5	B	A,C	
		1.0	1619	2.5		D,E	
74		0.8	1418	1.7	E	A,C	
		1.0	1428	1.7		D,E	
75	Beulah Lignite	1.2	1380	2.8	A	B	
		1.0	1391	2.8	C	D	
			1448			E	

Includes CCSEM samples for Runs 21-35

Figure 4.1.1 Temperature Profile for Illinois #6; Run 21

Figure 4.1.2 Temperature Profile for Beulah Lignite; Run 22

Figure 4.1.3 Temperature Profile for Eagle Butte; Run 23

Figure 4.1.4 Temperature Profile for Kentucky #9; Run 24

Figure 4.1.5 Temperature Profile for Kentucky #11; Run 27

Figure 4.1.6 Temperature Profile for Upper Freeport; Run 32

Figure 4.1.7 Temperature Profile for Upper Freeport; Run 35

be seen in Figures 4.1.5 through 4.1.7. These profiles were also similar to those from the previous set. These experiments were utilized to determine the overall ash behavior for these coals (Section 4.5) and the details are presented elsewhere (Gallagher, 1992).

Runs 36 through 40 were performed to determine the effect of temperature on ash formation. Run 39 (and the other experiments not mentioned here) utilized a coal, the Loy Yang, with very little ash and therefore was not part of this work. These experiments were primarily to determine the overall ash behavior of the various coals. Again, the data for the ash behavior analysis is presented in Section 4.5, but the experimental details (eg; temperature profiles and fraction oxide plots) are presented elsewhere (Gallagher, 1992).

The remaining experiments, Runs 47 through 75, were performed, in part, to study the dependence of the iron partitioning on temperature and stoichiometric ratio. Runs 47 and 48 were performed in conjunction with Jeff Moore from Physical Sciences Inc. (PSI) and Neal Gallagher. Moore collected particle size distributions with an in-situ particle measuring device. However, as this information was not used for this study, it will not be included (see Gallagher, 1992). Temperature profiles for these experiments can be seen in Figures 4.1.8 and 4.1.9.

Figure 4.1.8 Temperature Profile for Illinois #6; Run 47

Figure 4.1.9 Temperature Profile for Beulah Lignite; Run 48

Burn 56 utilized the Kentucky #11 coal under different mass loadings, and therefore different temperature profiles. Samples from this experiment were analyzed by Mössbauer analysis at both the University of Kentucky and the University of Arizona. AA analysis was also performed on these samples. The change in furnace mass loading resulted in approximately a 200 °C increase in the peak gas temperature as seen in Figure 4.1.10.

Runs 57 and 58 were designed to explore the effect of stoichiometric ratio on the iron partitioning. In each experiment the stoichiometric ratio was controlled by the addition of either nitrogen or oxygen. It was hoped that by keeping the total gas flowrate constant, the temperature profiles and residence times would be similar. However, Figures 4.1.11 and 4.1.12 show this was not the case. In addition, later experiments suggested there were severe leaks in the furnace. Due to the fact the furnace was run under a slight vacuum, these leaks caused excess air to be drawn into the furnace. Although the true furnace combustion conditions could be estimated as described in Chapter 3, there were some uncertainties caused by these leaks. Therefore, the data from these experiments were used as a guide, but needed to be confirmed in subsequent experiments.

Figure 4.1.10 Temperature Profile for Kentucky #11; Run 56

Figure 4.1.11 Temperature Profile for Kentucky #11; Run 57

Figure 4.1.12 Temperature Profile for Kentucky #11; Run 58

The experiments utilizing the Kentucky No. 9/Eagle Butte Blend were performed to obtain basic ash data for this mixture of coals. In addition, this set of experiments was used to compare the performance of two different impaction surfaces in the cascade impactor (see Section 4.2). Temperature profiles can be seen in Figures 4.1.13 and 4.1.14. The depressed temperature profiles (as compared to the other experiments) resulted from a lower coal feedrate for these experiments.

Runs 61 through 69 were performed to collect additional iron partitioning data for the Eagle Butte and Kentucky #9 coals. Unfortunately, equipment malfunctions and experimental errors didn't allow very many of these burns to be used. For example, in several of the experiments the gas probe was plugged with particles from the furnace, causing air to be drawn into any leaks. In other cases, insufficient sample was collected for analysis. The temperature profiles for these runs can be seen in Figures 4.1.15 through 4.1.23. The next two experiments, Run 70 and 71, utilized the Illinois #6 and Upper Freeport coals respectively. These two runs were also performed to obtain more iron partitioning data for these coals. Temperature profiles can be seen in Figures 4.1.24 and 4.1.25.

The final set of experiments explored the effect of stoichiometric ratio on the iron partitioning. The first 3 experiments, Runs 72 through 74, used the Kentucky #11 coals under various stoichiometric ratio and coal feedrates. The coal feedrate was set for the entire experiment while the air flow was changed to vary the

Figure 4.1.13 Temperature Profile for K9/EB Blend; Run 59

Figure 4.1.14 Temperature Profile for K9/EB Blend; Run 60

Figure 4.1.15 Temperature Profile for Eagle Butte; Run 61

Figure 4.1.16 Temperature Profile for Eagle Butte; Run 62

Figure 4.1.17 Temperature Profile for Eagle Butte; Run 63

Figure 4.1.18 Temperature Profile for Eagle Butte; Run 64

Figure 4.1.19 Temperature Profile for Kentucky #9; Run 65

Figure 4.1.20 Temperature Profile for Kentucky #9; Run 66

Figure 4.1.21 Temperature Profile for Kentucky #9; Run 67

Figure 4.1.22 Temperature Profile for Kentucky #9; Run 68

Figure 4.1.23 Temperature Profile for Kentucky #9; Run 69

Figure 4.1.24 Temperature Profile for Illinois #6; Run 70

Figure 4.1.25 Temperature Profile for Upper Freeport; Run 71

Figure 4.1.26 Temperature Profile for Kentucky #11; Run 72

stoichiometric ratio. In order to prevent air leakage into the furnace, the furnace was run under slightly positive pressure. Figures 4.1.26 through 4.1.28 show the temperature profiles for these experiments. The high temperature profile in Run 72 was caused by a high coal feedrate and preheating the primary air. The final experiment, Run 75, was very similar to Run 74 except that the Beulah Lignite coal was used. In this experiment samples were collected for stoichiometric ratios of 1.2, 1.0, and approximately 0.8. Unfortunately there was some difficulty burning this coal. Therefore the data could not be used. The temperature profiles for this experiment are shown in Figure 4.1.29.

Figure 4.1.27 Temperature Profile for Kentucky #11; Run 73

Figure 4.1.28 Temperature Profile for Kentucky #11; Run 74

Figure 4.1.29 Temperature Profile for Beulah Lignite; Run 75

4.2 AA Analysis of Ash

Atomic Absorption played a major role in determining the overall ash behavior and the iron behavior during combustion for the study coals. Most of the information for this purpose is discussed in Section 4.5. Additional information for those experiments can be seen in the PhD dissertation by Neal Gallagher (1992) or in the Project Final Report (Boni et al., 1992). Fraction oxide plots for those experiments utilizing AA, but not covered by Gallagher (1992) can be seen in Appendix A. For the iron partitioning work, however, the AA data was used primarily to explore the possibility of iron fume formation as proposed by Baxter and Mitchell (1992).

If an iron fume formed as proposed by Baxter and Mitchell (1992), a large fraction of the iron would be found in the small ($<0.2\ \mu\text{m}$) sizes. Therefore, the impactor data should show a large fraction of iron in the lower plates (plate 8 and the after filter). Figures 4.2.1 through 4.2.6 show, however, that very little iron is in the small sizes for the coals used in this study. In fact, most of the iron is found in the large size classes. This evidence suggests that iron fume does not form under the combustion conditions used in this work. Researchers at PSI were also unable to find evidence to support iron fume formation in their work (Helble, pers. comm.).

AA was also used in this work to analyze data for the EB/K9 Blend. The fraction oxide plots for this coal can be seen in Figure 4.2.7 and Figure 4.2.8. These

Figure 4.2.1 Iron Distribution in Ash from Beulah Lignite

Figure 4.2.2 Iron Distribution in Ash from Eagle Butte

Figure 4.2.3 Iron Distribution in Ash from Illinois No. 6

Figure 4.2.4 Iron Distribution in Ash from Kentucky No. 11

Figure 4.2.5 Iron Distribution in Ash from Kentucky No. 9

Figure 4.2.6 Iron Distribution in Ash from Upper Freeport

Figure 4.2.7 Fraction Oxide versus Impactor Stage for Run 59; Kentucky 9-Eagle Butte Blend

Figure 4.2.8 Fraction Oxide versus Impactor Stage for Run 60; Kentucky 9-Eagle Butte Blend

plots show some evidence of alkali and calcium enrichment in the small stages. These experiments were also used to test the suitability of polyethylene disks as the impactation substrate. Prior to these experiments the more expensive teflon filters used as the after filter (Chapter 3) were also used as the impactation substrate for the other plates. As can be seen in Figures 4.2.9 and 4.2.10 the mass distribution in the impactor is not appreciably affected by the change in impactation substrate. Therefore the less expensive polyethylene disks were used in subsequent experiments.

Figure 4.2.9 Ash Mass Distribution for Run 59; K9/EB Blend

Figure 4.2.10 Ash Mass Distribution for Run 60; K9/EB Blend

4.3 CCSEM Analysis of Ash

Computer Controlled Scanning Electron Microscopy (CCSEM) of collected ash samples was another analytical technique that received a great deal of attention in other aspects of the mineral matter project, but was only of limited use in this study. The information gleaned from CCSEM analysis of selected fly ash samples was used primarily to estimate the amount of inherent mineral matter in the coal

It was assumed from work described in Section 4.5 that, due to agglomeration, any ash originating in the char matrix would contain small amounts of all the species found inside the matrix. For example, inherent pyrite combines with inherent silicates forming ash particles containing iron, silicon, and aluminum. The extraneous material, as previously mentioned, would not be likely to interact with the inherent material or itself. The extraneous material, then, was defined as that material that did not contain appreciable amounts of other species. The extraneous silicates, for example, was defined as that containing less than 10 mole percent (oxygen free basis) of iron or calcium (in the case of those coals with finely divided calcium). Extraneous iron was defined as the fraction of iron denoted by CCSEM 'as oxide' (at least 90% iron, oxygen free basis). In addition, as the CCSEM analysis was only performed on the ash from plate 1 and the cup of the impactor ($>9\mu\text{m}$) for most experiments, it was assumed that the remaining ash ($<9\mu\text{m}$) was initially inherent. The average fraction of both the total ash and iron mass captured in the analyzed

fraction was determined from previous experimental data. Figure 4.3.1 shows a schematic of these calculations. The results can be seen in Table 4.3.1.

Figure 4.3.1 Schematic for Calculation of Inherent Silicate and Iron

Calculation of Percent Inherent Silicate

Calculation of Percent Inherent Iron

Table 4.3.1 Input Parameters

COAL	Illinois #6	Kentucky #11	Kentucky #9	Upper Freeport	Beulah Lignite	Eagle Butte
g ash/g coal	0.0860	0.2030	0.1430	0.232	0.096	0.048
MF Silicates	0.6330	0.704	0.808	0.788	0.713	0.879
MF Pyrite	0.2800	0.2400	0.1600	0.1800	0.2600	0.0400
MF Ext. Sil. (CCSEM)	0.3687	0.1880	0.2230	0.2260	0.1400	0.1820
MF Ext. Pyr. (CCSEM)	0.4300	0.3100	0.3540	0.1600	0.4200	0.2500
MF Total Ash on plate 1 + cup	0.9300	0.9500	0.9000	0.8840	0.9000	0.6900
MF Total Iron on plate 1 + cup	0.9300	0.9500	0.9000	0.8840	0.9000	0.6900
Inh. Sil. * (CCSEM)	0.0344	0.1160	0.0898	0.1415	0.0589	0.0345
Inh. Pyrite * (CCSEM)	0.0137	0.0336	0.0148	0.0351	0.0145	0.0014
Ext. Pyrite * (CCSEM)	0.0104	0.0151	0.0081	0.0067	0.0105	0.0005
Inh. Sil * (includes <9um)	0.0358	0.1174	0.0924	0.1463	0.0598	0.0369
Inh. Pyrite * (based on CCSEM & not caught Im1 + cup)	0.0145	0.0344	0.0156	0.0359	0.0155	0.0016
g ext. pyr/g coal	0.0096	0.0143	0.0073	0.0059	0.0094	0.0003

* g/g coal

4.4 Mössbauer Analysis of Ash

Due to its ability to distinguish between iron as oxide and iron as a glass, as discussed in Chapter 3, Mössbauer analysis played a very important role in this study. The initial samples were sent to the University of Kentucky for analysis. Later samples were analyzed at the University of Arizona.

The Kentucky group distinguished between iron as glass, both as Fe^{3+} and Fe^{2+} , and iron as oxide, both oxidation states. At the University of Arizona there was insufficient resolution to distinguish between Fe^{3+} and Fe^{2+} in the glass. Instead, the glass was typically defined as a doublet in the approximate center of the spectrum (see Figure 4.4.1). The oxide forms were identified positively as a set of split lines. For pyrrhotite another set of lines were found as shown in Figure 4.4.1. The raw data at the University of Arizona was then converted to fractions of iron in each phase utilizing a fitting program, written by Dr. Roy Emrick, to find the lines and determine the area under each curve. The results from this analysis can be seen in Tables 4.4.1 (from University of Kentucky) and 4.4.2 (University of Arizona). It should be noted that samples from the Kentucky #11 Run 56 were analyzed in both facilities with reasonably similar results (Tables 4.4.1 and 4.4.1). The individual spectrum can be seen in Appendix B.

It was noted that the fraction of iron as glass seemed to increase as the ratio of inherent silicate to pyrite increased. This would be expected as there would be more

silicate for the pyrite to interact with to form any glassy phases. There was also some evidence that the fraction iron as glass and pyrrhotite increased with decreasing stoichiometric ratio. This is probably due to the increase in unoxidized pyrrhotite.

Figure 4.4.1 Mössbauer Spectrum For Run 73B With Peaks Labeled

Table 4.4.1 Iron Distribution (Mole %) in Ash (University of Kentucky)

ID	Coal	Fe ₃ O ₄	Fe ₂ O ₃	Fe ²⁺ Glass	Fe ³⁺ Glass
21A	Ill. #6	84	-	-	16
22A	Beulah Lig.	71	-	5	24
23A	Eagle Butte	46	-	-	54
27E	Kent. #11	67	8	14	12
32F	Upper Freeport	67	3	13	18
35E		54	6	14	26
47B	Ill. #6	62	19	-	19
47D		68	-	15	17
47H		68	-	10	22
48B	Beulah	63	-	-	37
48F	Lignite	62	-	-	38
51B	Ill. #6 SOAP*				23
56A	Kent. #11	58	19	-	23
56D		62	8	14	16
57A**		53	4	24	-
58C		50	11	12	27

* 77% reported as spm oxide

** contained 19% pyrite and fe sulfide

Table 4.4.2 Iron Distribution (Mole %) in Ash (University of Arizona)

ID	Coal	Fe ₃ O ₄	Fe ₂ O ₃	Glass	Pyrrhotite
56C	Kent. #11	61.6	15.4	23	-
56F		2.3	60.4	37.3	-
61B	Eagle Butte	-	27.3	72.7	-
64A		-	18.8	81.2	-
67C	Kent. #9	18.9	58.8	22.3	-
68		-	74.6	25.5	-
69A		-	63.9	36.1	-
69C		-	61.6	38.4	-
70B	Ill. #6	64.8	9.6	25.6	-
70C					
71	Up. Free.	-	51.4	48.6	-
72	Kent. #11	-	23.6	33.2	43.2
73B		34.0	-	43.8	22.2
73E		64	-	36.0	-
74C		11.6	19.0	47.8	21.6
74E		54.2	-	42.0	3.8

4.5 Iron and Ash Behavior During Combustion

One of the initial goals of this work was to determine the dominant mechanism for fly ash formation during pulverized coal combustion. Potential mechanisms include vaporization, coagulation/agglomeration (noted as agglomeration), and fragmentation. Each of these mechanisms causes a net shift in the fly ash size distribution as compared to the original mineral matter. For example, vaporization causes more of the ash mass to occur in the very small size ranges. Fragmentation also causes a net decrease in the particle sizes, although not to such a great degree as vaporization. Agglomeration, on the other hand, causes a net increase in particle size. In order to determine which mechanism governs the fly ash behavior, comparisons were made between the mass-size distribution of the ash (from impactor data) and the mass-size distribution of the original mineral matter (from CCSEM). A similar comparison was made to determine the net behavior of iron in the ash.

4.5.1 Data Manipulation

Before using the impactor data to determine the dominant ash formation mechanism, it is important to ensure that the data is being interpreted correctly. Potential problems arise if the impactor does not represent the true mass-size distribution or if a size change occurs that is not attributable to the previously mentioned mechanisms. If, for example, a pyrite particle (S.G. 5.0) reacts to form a iron sulfate

particle (S.G. 2.5) of the same mass, would the expansion (not due to the previously mentioned mechanisms) cause an appreciable shift in the mass-size distribution in the impactor? To answer this question a series of pyrite particle sizes were chosen (see Table 4.5.1) and the sizes for particles of different density, but the same mass as the original pyrite, were calculated. The impactor cut off diameters were also corrected for the density differences (Table 4.5.2) as shown by Marple and Willeke (1979). By assuming the Cunningham correction factor does not change significantly, the true particle cut off diameter can be found by dividing the impactor cut off diameter by the square root of the true specific gravity. Comparing the particle sizes with the true particle cut off diameters (see Table 4.5.3) shows that particles with the same mass are captured on the same plate as long as the density differences are relatively small (S.G. 5.0 to 2.5). Therefore, for relatively small density changes there is not an appreciable change in the mass-size distribution.

Another potential problem in using the impactor data arises the technique used to analyze the ash samples. The analysis technique used, Atomic Absorption, only determines the mass of each element on each stage, not the mineral form of each element. Therefore the impactor cut off diameters (S.G. assumed to be 1) can not be corrected for the true density as described above. In order to minimize this problem a "worst case" was assumed such that all particles had a specific gravity of 5. The impactor cut off diameters were then corrected as described above. As typical ash specific gravities are approximately 2.5, it is reasonable to assume that the true

size-mass distribution should lie between the distribution from the impactor and the "worst case" distribution.

Table 4.5.1.1 Change of Particle Size with Density

Compound	S.G	D _p (μm)				
Pyrite	5.00	0.50	1.00	2.00	3.00	4.00
Fe ₂ O ₃	5.12	0.50	0.99	1.98	2.98	3.97
Fe ²⁺ Sulfate	2.50	0.63	1.26	2.52	3.78	5.04
FeS	4.84	0.51	1.01	2.02	3.03	4.04

Note: Pyrite Mass Assumed Constant

Table 4.5.1.2 Corrected Impactor Cut Off Diameters (μm)

S.G	1.00	2.50	4.84	5.00	5.12
Plate 1	9.00	5.69	4.09	4.02	3.98
Plate 2	5.80	3.67	2.64	2.56	2.56
Plate 3	4.70	2.97	2.14	2.10	2.08
Plate 4	3.30	2.09	1.50	1.48	1.46
Plate 5	2.10	1.33	0.95	0.94	0.93
Plate 6	1.10	0.70	0.50	0.49	0.49
Plate 7	0.65	0.41	0.30	0.29	0.29
Plate 8	0.43	0.27	0.20	0.19	0.19
AF	<0.43	<0.27	<0.20	<0.19	<0.19

Table 4.5.1.3 Capture Plates for Various Sized Particles

S.G.	$D_p (\mu m)^*$	Impactor Plate
5.0	0.50	6
2.5	0.63	7
1.0	0.86	7
5.0	1.00	5
2.5	1.26	6
1.0	1.71	6
5.0	2.00	4
2.5	2.52	4
1.0	3.42	4
5.0	3.00	2
2.5	3.78	2
1.0	5.13	3
5.0	4.00	2
2.5	5.04	2
1.0	6.84	2

* Calculated from Density Change of Pyrite as Seen in Table 4.5.1

4.5.2 Discussion of Mass-Size Distributions for Study Coals

The mass fraction plots for the Kentucky No. 11 coal can be seen in Figures 4.5.2.1 and 4.5.2.2. The overall ash mass distribution is shifted toward the larger size ranges as compared to the original mineral matter. This shift suggests that agglomeration is the predominant mechanism for ash formation. Researchers at PSI reached the same conclusion after viewing a similar plot (Figure 4.5.2.3). The iron in the original minerals, predominantly pyrite, was also shifted to the larger size ranges during the combustion process as shown in Figures 4.5.2.4 and 4.5.2.5. This shift suggests that the iron agglomerates with other ash constituents (predominantly silicon and aluminum). The PSI researchers, on the other hand, show evidence of some pyrite fragmentation (Figure 4.5.2.6). It should be noted here that they defined the pyrite concentration as that from CCSEM analysis of the coal. Mossbauer analysis showed the pyrite concentration to be significantly higher. The discrepancy was attributed to signals from surrounding silicate particles overlapping those of the pyrite in the CCSEM analysis (Boni et al., 1990). In addition, the iron ash distribution they present is for particles containing predominantly iron oxide. Thus, they followed the evolution of pyrite particles that were unaffected by the surrounding silicates while discounting those that coagulated/agglomerated with silicates. This study, on the other hand, determined the overall behavior of all the iron species.

Figure 4.5.2.1 Ash Mass Distribution for Kentucky No. 11; Average of Runs 27 and 28

Figure 4.5.2.2 Ash Mass Distribution for Kentucky No. 11; Run 37

Figure 4.5.2.3 Ash Mass Distribution for Kentucky No. 11 from PSI (Boni et al., 1990)

Figure 4.5.2.4 Iron Mass Distribution for Kentucky No. 11; Average of Runs 27 and 28

Figure 4.5.2.5 Iron Mass Distribution for Kentucky No. 11; Run 37

Figure 4.5.2.6 Iron Mass Distribution for Kentucky No. 11 from PSI (Boni et al., 1990)

The next coal studied, the Kentucky No 9, showed cumulative mass fraction trends similar to those from the Kentucky No. 11. Figures 4.5.2.7 and 4.5.2.8 show a shift toward the larger particle sizes, again suggesting agglomeration to be the predominant mechanism. This conclusion was also substantiated by researchers at PSI (Figure 4.5.2.9). The iron behavior was also similar to that in the Kentucky No. 11, although the shift is not nearly as great (Figures 4.5.2.10 and 4.5.2.11). The smaller shift indicates that if agglomeration does take place it does so to a lesser degree than in the Kentucky No. 11. Figure 4.5.2.12 shows that the PSI group also found a small, if any, shift.

Agglomeration, was also suggested as the dominant mechanism for ash and iron ash formation in the Illinois 6 coal (see Figures 4.5.2.13 and 4.5.2.14). Research by the PSI group also supports this hypothesis as shown in Figure 4.5.2.15. In addition, the PSI group reports, "Initially, 75 percent of the iron was present in a silicon free state (by CCSEM; Mossbauer levels higher), while at the conclusion of combustion, 72 percent of the iron was associated with silicate particles." (Boni et al, 1990). This presents further evidence that the iron agglomerates with the silicates.

The next coal studied was the Eagle Butte. The cumulative mass fraction and cumulative mass concentrations distributions for the ash (Figures 4.5.2.16 and 4.5.2.17) showed very little change between the ash at the conclusion of combustion

Figure 4.5.2.7 Ash Mass Distribution for Kentucky No. 9; Average of Runs 17 and 18

Figure 4.5.2.8 Ash Mass Distribution for Kentucky No. 9; Run 36

Figure 4.5.2.9 Ash Mass Distribution for Kentucky No. 9 from PSI (Boni et al., 1990)

Figure 4.5.2.10 Iron Mass Distribution for Kentucky No. 9; Average of Runs 17 and 18

Figure 4.5.2.11 Iron Mass Distribution for Kentucky No. 9; Run 36

Figure 4.5.2.12 Iron Mass Distribution for Kentucky No. 9 from PSI (Boni et al., 1990)

Figure 4.5.2.13 Ash Mass Distribution for Illinois No. 6; Average of Runs 19 and 20

Figure 4.5.2.14 Iron Mass Distribution for Illinois No. 6; Average Runs 19 and 20

Figure 4.5.2.15 Ash Mass Distribution for Illinois No. 6 from PSI (Boni et al., 1990)

and the original minerals. The PSI group found the same results, although a slight decrease in size was noted (Figure 4.5.2.18). The PSI group attributes this slight shift to the small sizes to a possible coalescence of finely divided calcium. The pyrite and calcite levels were low so fragmentation of these species were neglected. Figures 4.5.2.19 and 4.5.2.20 show that the cumulative mass distributions of the iron shift to the smaller size ranges with respect to the original pyrite distribution. This evidence would indicate that, while the iron concentrations are low enough for the fragmentation to be neglected on the overall mass distribution, fragmentation does seem to occur.

For the Upper Freeport coal the cumulative mass distribution (Figure 4.5.2.21) again indicate agglomeration. However, the PSI group found a lack of evidence to support this mechanism. Instead they found a decrease in the size. It should be noted, however, that the impactor data only goes up to a size of 9 microns while the CCSEM data goes significantly higher. In the region (less than 9 microns) where the sizes are similar, the plot shown in Figure 4.5.2.22 does correlate fairly well with those from the impactor data. Due to the relatively high amounts of nonpyritic iron in the original minerals, it was not possible to look at the iron behavior with respect to the impactor data. The PSI group, however, showed evidence of pyrite fragmentation (see Figure 4.5.2.23).

Figure 4.5.2.16 Ash Mass Distribution for Eagle Butte; Average of Runs 15 and 16

Figure 4.5.2.17 Ash Mass Distribution for Eagle Butte; Run 40

Figure 4.5.2.18 Ash Mass Distribution for Eagle Butte from PSI (Boni et al., 1990)

Figure 4.5.2.19 Iron Mass Distribution for Eagle Butte; Average of Runs 15 and 16

Figure 4.5.2.20 Iron Mass Distribution for Eagle Butte; Run 40

Figure 4.5.2.21 Ash Mass Distribution for Upper Freeport; Average of Runs 32 through 35

Figure 4.5.2.22 Ash Mass Distribution for Upper Freeport from PSI (Boni, 1990)

Figure 4.5.2.23 Iron Distributions for Upper Freeport from PSI (Boni et al., 1990)

The final coal studied was the Beulah Lignite. The cumulative mass distributions for the ash, Figures 4.5.2.24 and 4.5.2.25, showed little or no change in the size distribution. Comparison of the CCSEM results from the impactor to those from PSI yields a fairly good correlation between the two (Figure 4.5.2.26). The PSI data (Figure 4.5.2.27) shows that the overall size tends to decrease with respect to the initial minerals. In addition, the data shows that this trend increases with percent oxygen in the system (particle temperature). The high amount of pyrite (25% of the mineral matter) may provide some explanation for this behavior. The iron distributions for both the impactor data (Figures 4.5.2.28 and 4.5.2.29) and the PSI data (Figure 4.5.2.30) show strong evidence of fragmentation. This fragmentation may cause the overall shift to smaller sizes seen in the CCSEM results from both groups.

In conclusion, the cumulative mass fraction distributions were used to suggest dominant formation mechanisms for the overall ash formation and iron ash formation for various coals in this study. These results were found to be consistent with those from other researchers. However, as no distinction was made between the inherent and extraneous mineral matter, these mechanisms are only representative of the ash as a whole. The presence of large amounts of extraneous pyrite, for example, may cause the mass distributions to show fragmentation as the dominant mechanism, while the inherent minerals agglomerate. Therefore, the mechanisms described here are used only to define the overall ash and iron behavior.

Figure 4.5.2.24 Ash Mass Distribution for Beulah Lignite; Average of Runs 13 and 14

Figure 4.5.2.25 Ash Mass Distribution for Beulah Lignite; Run 38

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Comparison of PSIT and UA ash particle size distributions
obtained from Beulah lignite combustion.

Figure 4.5.2.26 Comparison of UA data and PSI data (Boni et al., 1990)

Mineral and ash particle size distributions by CCSEM for Beulah lignite at 1500 K, 7 and 21 percent O₂. Error bars represent 2σ confidence limits; precision at 7 percent O₂ (not shown) comparable to 21 percent O₂.

Figure 4.5.2.27 Ash Mass Distribution for Beulah Lignite from PSI (Boni et al., 1990)

Figure 4.5.2.28 Ash Mass Distribution for Beulah Lignite; Average of Runs 13 and 14

Figure 4.5.2.29 Iron Mass Distribution for Beulah Lignite; Run 38

Figure 4.5.2.30 Iron Mass Distribution for Beulah Lignite from PSI (Boni et al., 1990)

4.5.3 Ash Mass Concentration Distributions

Although the work discussed in the previous section used the cumulative ash, and iron, mass distributions to determine the dominant behavior, another type of distribution could also have been used. The ash, and iron, mass concentration distributions in the flue gas, for example, could have been used to determine the dominant behavior. These distributions (typical plots can be seen in Figure 4.5.3.2 and 4.5.3.3) were created as described in Figure 4.5.3.1. First the total ash mass concentration for each experiment was calculated using the coal feed rate, the flue gas rate and the Foster Wheeler coal analysis. The total mass concentration was then recalculated using the total mass collected in the impactor and the total flue gas sampled. These two total concentrations were often very different (see Table C.1 in Appendix C). Reasons for these differences could not be determined but may include losses to the wall and sampling errors. To compare ash mass concentration distributions and the original mineral matter concentration distribution, a total mass concentration must be assumed (the Foster Wheeler was used in this case). This total mass concentration was multiplied by the ash mass distribution in the impactor to get the ash mass concentration distribution. The original mineral matter concentration distribution was calculated using the total mass concentration and the mineral matter distribution from CCSEM. Although these plots present more information about each experiment, they tend to obscure the mass-size distribution. Therefore, they were not used to determine the overall ash and iron behavior.

Figure 4.5.3.1 Schematic for Ash Mass Concentration Calculations

Ash Data Manipulation for Mass Concentration Distributions

Mineral Data Manipulation for Mass Concentration Distributions

Figure 4.5.3.2 Ash Mass Concentration Distribution for Beulah Lignite; Run 38

Figure 4.5.3.3 Ash Mass Concentration Distribution for Kentucky 11; Run 37

4.6 Iron-Silicate Interactions During Coal Combustion

One of the major goals of this project was to determine the important mechanisms for iron-silicate interactions during combustion. In order to achieve this goal, ash samples from the study coals were analyzed by both Mössbauer and CCSEM. When the results were compared (Table 4.6.1) there was a surprising discrepancy between the two techniques. For example, for the Illinois No. 6 ash Mössbauer analysis identified approximately 84 % of the iron as iron oxide. The CCSEM data , however, indicated that only 43% of the iron was found as "pure iron" (defined as containing a minimum of 90% iron on an oxygen free basis). Two possible mechanisms were hypothesized to explain this discrepancy (see Figure 4.6.1).

The first hypothesis suggested that iron and silicates exists as a melt in the combustion zone. Subsequent cooling would then cause crystallization of iron oxide out of the melt, resulting in iron oxide crystals embedded in a glassy silicate matrix. The second hypothesis suggested that a discrete iron oxide particle could agglomerate with discrete silicate particles. In both cases the CCSEM would "see" the agglomerate as a single large particle containing silicon and iron. The Mössbauer, on the other hand, would still recognize the iron oxide as discrete particles (eg: not chemically bound to the silicates). Thus, the CCSEM would indicate a lower "pure iron" percentage than the Mössbauer. In order to differentiate between these two mechanisms, a number of analytical tools were utilized on ash from two coals.

Table 4.6.1 Comparison of Iron Analysis for Ash from Various Coals

Coal	% Fe Oxide Mössbauer	% Fe Oxide (CCSEM)
Illinois #6	84	43
Beulah Lignite	71	42
Eagle Butte	46	25
Kentucky 11	75	31
Upper Freeport (Run 32)	70	16
Upper Freeport (Run 35)	60	*****

Figure 4.6.1 Proposed Iron-Silicate Interaction Mechanisms During Combustion

The first analytical tool used to differentiate between the proposed mechanisms was an SEM coupled with an X-Ray detector. Approximately 11 particle agglomerates from a Beulah Lignite ash sample were analyzed. Individual particles in each agglomerate were analyzed and their iron concentrations (relative EDX peak height) were compared. Of the 11 particles analyzed, only one showed any evidence of an iron oxide particle agglomerated with silicate particles. In this agglomerate a large particle was very enriched in iron as compared to other particles in the agglomerate. However, other agglomerates analyzed were found to contain either no appreciable iron or only a small, relatively constant, iron concentration. These findings would seem to support both proposed hypothesis to some degree, and thus were somewhat inconclusive.

When it became apparent that the EDX-SEM work alone was not sufficient to determine which mechanism may be dominant, a new technique, XRD (X-Ray Diffraction) was utilized to confirm the presence of iron oxide crystals. This technique involved spreading a small amount of ash (collected from the ash trap of an Illinois No. 6 run) on a glass or plastic slide. The sample was then bombarded with x-rays at various angles. The intensity of the x-rays emitted for various angles allows the determination of the crystalline form of a species. The spectra shown in Figure 4.6.2 when compared with Table 4.6.2 (note: matrix effects may cause the peaks to be shifted slightly from the table value), indicate that iron oxide crystals were indeed present.

Figure 4.6.2 XRD Spectrum from Illinois No. 6 Ash Trap Sample

Table 4.6.2 Major XDS Angles for Magnetite and Hematite

Species	Angle (degrees)	Magnitude
Hematite	33.15	100
	35.61	70
	40.86	20
Magnetite	30.10	30
	35.42	100
	43.06	20

When the XRD data indicated that, at least for the Illinois No. 6 coal, iron oxide particles did indeed exist, Auger mapping and sputtering was utilized to attempt to find the crystals in the silicate lattice. However, no appreciable iron was found in any of the particles analyzed by this method so the next method was utilized.

The next analytical tool utilized was a TEM (Transmission Electron Microscopy) at the High Resolution Electron Microscopy (HREM) Facility at Arizona State University. A small amount of ash (collected from the same ash sample used in the XRD analysis above) was introduced into a small amount of propanol and ground into a fine powder. The maximum thickness that can be used in this technique is on the order of 0.1-0.2 μm . A drop of the slurry was then placed on a carbon membrane supported by a copper grid and allowed to dry. The sample was then analyzed.

The initial investigations, conducted by Roger Graham and Larry Bool on the Philips

400T at the HREM facility found the following;

- (1) large glassy particles (fairly common)
- (2) clusters of plate-like crystals, beam sensitive (easily damaged by the beam), (common)
- (3) large particles of beam stable material, giving convergent beam electron diffraction patterns (CBED) with good detail, (uncommon)
- (4) composite particles of small, needle-like, beam stable crystalline material embedded in a glassy matrix (rare)

The following session, again conducted by Roger Graham and Larry Bool on the FEG Philips 400ST at the HREM facility found the following;

- (1) the large glassy particles contained predominantly Si, Al, Ca, K, Fe
- (2) the clusters of plate-like particles were predominantly Ca, S, Si
- (3) the large particles of beam stable material were almost completely pure Fe
- (4) the glassy matrix of the composite particles was made up of Al, Si, Ca, Fe while the small needle-like particles contained the same species but contained less iron and more aluminum than the matrix
- (5) a group of small needle-like particles (not in a matrix) not noted in the initial investigation contained almost pure Ca, may have been a result of water absorption by a hygroscopic Ca species during the layover between sessions.

In addition, the particles mentioned in (3) above were assumed to have come from a discrete iron oxide particle as the typical dimensions were 1 μm by 0.3 μm . The CBED spectrum collected from this particle also identified it as Fe_2O_3 . Thus, this evidence would seem to support an agglomeration mechanism as the only iron

crystals found were determined to have been part of a discrete particle. This analysis was also performed on ash from Beulah Lignite with similar results.

After the TEM results were obtained, the particles were analyzed utilizing an X-Ray mapping routine. An agglomerate was analyzed and mapped for Fe, Si, Al, Ca, Mg, K, Na. Areas of apparently enriched iron were then magnified and reanalyzed until the source of the iron enrichment was determined. In almost all cases the source of enrichment was one or more "pure" iron particles (as evidenced by the EDX maps) agglomerated with silicate particles. For example, in the agglomerate shown in Figure 4.6.3 there are particles containing primarily iron agglomerated with both iron-silicon and silicate particles (Figures 4.6.4 and 4.6.5). This behavior can be seen for the Beulah Lignite ash in Figures 4.6.6 through 4.6.10. Both the low probability of iron particles of these sizes impacting on the first impactor plate (much less than 10%), and the relatively low particle temperatures (approximately room temperature) during size classification indicate that the agglomerations were formed during the combustion process, not as an artifact of the sampling technique. Therefore, this evidence strongly suggests that the agglomeration mechanism was the dominant pathway for iron-silicate interactions within the char matrix.

Figure 4.6.3 SEM Micrograph of Particle Agglomerate from Illinois No. 6 Ash

Figure 4.6.4 EDX Iron Map of Particle Agglomerate from Illinois No. 6 Ash

Figure 4.6.5 EDX Silicon Map of Particle Agglomerate from Illinois No. 6 Ash

Figure 4.6.6 SEM Micrograph of Particle Agglomerate from Beulah Lignite Ash

Figure 4.6.7 SEM Micrograph of Particle Agglomerate from Beulah Lignite Ash Under Higher Magnification

Figure 4.6.7 EDX Iron Map of Particle Agglomerate from Beulah Lignite Ash

Figure 4.6.9 EDX Silicon Map of Particle Agglomerate from Beulah Lignite Ash

Chapter 5

5. Mathematical Model of Iron Partitioning

Although iron has long been known to be a major contributor to slagging and fouling, most of the modelling done to date has focussed on the behavior of extraneous pyrites during combustion. The inherent pyrite, on the other hand, has been treated primarily on a qualitative basis as part of overall ash behavior studies. For example, studies have been performed on synthetic ashes to determine the stickiness of the ash on various substrates. Other studies have burned coals under various conditions to determine the sticking properties of the resulting ash. In these studies iron represents only one of the many variables the investigators may be exploring.

This work represents one of the first times a quantitative model has been developed to predict the fate of iron during combustion. In the previous chapter it was shown that agglomeration during burnout is the dominant mechanism for iron-silicate interaction during combustion. This mechanism, in conjunction with the mechanism for extraneous pyrite oxidation, has now been used to propose a comprehensive model to quantitatively predict the partitioning of the original iron between slag enhancing, sticky, phases and crystalline phases.

Section 5.1: Mechanistic Description of Model

The proposed model is based on a competition, shown schematically in Figure 5.1.1, between iron-silicate interactions (glass formation) and pyrite oxidation/solidification. Glass formation occurs primarily by particle coagulation (particle interactions in the gas phase) or iron-silicate agglomeration-sintering (particle interactions on the char surface). Although iron fume may also mix with the silicates, this mechanism is neglected due to lack of evidence for fume formation (see Section 4.2).

For this model it is assumed that the extraneous ash does not interact appreciably with the inherent ash or itself (i.e., no coagulation). Due to the relatively large particle sizes involved (greater than $50\mu\text{m}$), and the low terminal settling velocities (relative to furnace velocities), coagulation probabilities are minimized (Hinds, 1982). Therefore it is possible to model the partitioning of the extraneous and inherent pyrite independently.

The inherent pyrites are affected by both the char and the other materials in the char. Initially the inherent ash material is assumed to be homogeneously distributed throughout the char matrix. While inside the matrix the ash may melt and decompose but may not move from its initial position in the matrix (no capillary creep). As the char is burned away, inherent (inside the carbon matrix) pyrrhotite and silicate particles are exposed as shown in Figure 5.1.2. Once exposed, the

Figure 5.1.1 Iron Partitioning Pathways

pyrrhotite can either oxidize by the same mechanism as the extraneous pyrrhotite (Figure 5.2.1), or mix with the silicates. Iron oxide formed is either molten or solid, depending on the particle temperature. Glassy material is formed when molten silicates contact and sinter with either molten iron oxide or pyrrhotite. By modelling the glass formation and the pyrrhotite oxidation, the amount of inherent iron in each of the major phases can be predicted.

Predicting the partitioning of the extraneous iron is somewhat simpler as there is no glass formed (no coagulation). The partitioning, then, is based on the oxidation of the pyrrhotite as proposed by Srinivasachar (1989), Figure 5.2.1, and the solidification of the resulting oxide. The fraction of the original iron, inherent and extraneous, in slagging and fouling enhancing phases (ϕ) can therefore be determined by combining the two independent models.

Figure 5.1.2 Pathway for Ash Movement to Surface

5.2 Iron Oxide Formation

The iron oxide reaction pathway utilized by this model was similar to that presented by Srinivasachar et. al. (1989). The pathway, Figure 5.2.1, was used as described, with a few simplifications, for the extraneous pyrite. For the inherent pyrite, however, the mechanism was modified somewhat. This modification was necessary to take into account the effect of the carbon matrix on the pyrite oxidation.

The pyrite, inherent and extraneous, initially decomposes to pyrrhotite at approximately 800 K. Unlike the extraneous pyrite, however, the inherent pyrite does not begin to oxidize until it is exposed by the receding char surface (Brink et al, 1992). Both forms of pyrrhotite oxidize according to Equation 1, where SA_{pyr}

$$\frac{d(Fe_3O_4)}{dt} = k_o C_{mol-mass} SA_{pyr} \left(\frac{P_{O_{2s}}}{RT_g} \right) \quad (1)$$

$$SA_{pyr} = (Fe_{0.877}S) \frac{3}{r_{pyr} \rho_{pyr}} \quad (2)$$

(inherent) is defined by Equation 2. $C_{mol-mass}$ represents the conversion factor for moles O_2 to mass Fe_3O_4 . The parameter k_o is the overall mass transfer/reaction coefficient as given by Equation 3 (Srinivasachar, 1989). If the particle temperature is less than the pyrrhotite melting point (1356 K) the oxidation kinetics

Figure 5.2.1 Oxidation Pathways for Inherent and Extrinsic Pyrite

$$\frac{1}{k_o} = \frac{1}{k_l} + \frac{1}{k_m} + \frac{1}{K_p} \quad (3)$$

are given by Equation 4 using the appropriate particle temperature (inherent or extraneous). The parameters, K_{p0} and E_p , were $5 \times 10^9 \text{ cm sec}^{-1}$ and 150 kJ mole^{-1} as proposed by Srinivasachar et al. (1989) from work by Asaki et al. (1985).

$$K_p = K_{p0} \exp\left(\frac{-E_p}{RT_p}\right) \quad (4)$$

The gas mass transfer coefficient (k_m) is that given by equation 5 using the

$$k_m = \frac{D}{r_{extpyr}} \quad (5)$$

appropriate particle radius (inherent or extraneous). For the extraneous particle it is assumed that the particle is falling at approximately the same rate as the gas and, thus, 'sees' a stagnant fluid. The inherent size dependence is due to the assumption that the entire pyrite particle is inside the diffusion film for the char. For this reason, the oxygen partial pressure used in equation 1 for the inherent pyrrhotite is $P_{O_{2s}}$ rather than P_{O_2} .

The solid, or liquid, mass transfer coefficient used for this work was also proposed by Srinivasachar et al. (1989). This coefficient depends on several unknown parameters, such as the recirculating rate inside the particle and liquid phase

diffusivities. Therefore the parameter, k_p , was fit to existing data by Srinivasachar et al. (1989) according to Equation 6. The fit for this parameter may be missing some important information, but was found to be sufficient in most cases for this work.

$$k_l = \begin{cases} 0.75k_m & T_p \geq 1450K \\ 0.30k_m & T_p < 1450K \end{cases} \quad (6)$$

For temperatures greater than the melting point, the iron oxide formed by this point melts with the pyrrhotite to form an Fe-O-S melt. Oxidation of this melt is assumed to be transport limited (reaction kinetics are sufficiently fast to neglect $1/K_p$) for both the inherent and extraneous pyrrhotite as suggested by several investigators (Srinivasachar, 1989, Asaki et al., 1985, Jorgensen, 1981a, 1981b). This assumption leads to a melt oxidation rate that is relatively insensitive to particle temperatures.

The products of these reactions can be either liquid or solid depending on the particle temperature. Although the melting point of magnetite is 1870 K, it has been suggested that the melt must supercool as much as several hundred degrees prior to crystallization (Jorgensen, 1981). For this modeling a value of 1600 K (Srinivasachar, 1989) was assumed for crystallization of these melts.

The final important parameter for iron oxidation is the amount of pyrrhotite, ($\text{Fe}_{0.877}\text{S}$), on the surface. In this case the surface is treated as a batch reactor with an input stream (Equation 7). The mass of pyrrhotite on the surface depends on the

$$(Fe_{0.877}S) = \{(CHAR)_0 - (CHAR)\} MF_{pyr} - \frac{(G)}{1+y} - \frac{(Fe_3O_4)}{0.827} \quad (7)$$

amount of carbon burned away, the amount of iron oxide formed, the amount of iron oxide and pyrrhotite consumed by glass formation. Although the mass of iron captured per mass of glass can vary depending on iron solubility in the slag, a set of mass based reactions (Equations 8 and 9) was proposed to complete the mass balance. The parameter, y , represents a uniform fit parameter for the mass of silicate consumed during glass formation (for all coals). In this work, this parameter was found to be 8.1 (mass units are arbitrary).

In addition, it is necessary to balance the amount of molten iron oxide on the surface due to its ability to take part in glass formation. This balance is performed by removing iron oxide formed at temperatures less than 1600 K from the system while allowing iron oxide formed at temperatures greater than 1600 K to remain in the system until the temperature drops below 1600 K. In this manner molten iron oxide is available for capture by the silicates.

5.3 Glass Formation

Iron rich silicate melts are formed either by melting iron rich clays or by the coalescence of iron and silicate particles as shown in Figure 5.3.1. For glassy (ash type) particles Kuczynski (1949, 1956) showed that viscous flow is the dominant mechanism for coalescence. The surface tension forces 'pull' the molten particles together, causing viscous flow. Early sintering work (Frenkel, 1945) showed that the coalescence of particles by viscous flow can be described in terms of the particle size, the melt viscosity, and surface tension. The rate of coalescence, is directly proportional to the melt surface tension and inversely proportional to the viscosity and particle size.

Based on this viscous flow mechanism, a glass formation rate was proposed as follows:

$$\begin{array}{lcl} \text{Glass} & & \text{Rate at Which Iron} \\ \text{Formation} & = & \text{and Silicate Particles} \\ \text{Rate} & & \text{in Contact Sinter} \end{array} \bullet \begin{array}{l} \text{Probability of Contact} \\ \text{Between Iron and} \\ \text{Silicate Particles} \end{array}$$

The formation rate is defined mathematically by Equation 10. X_g represents the probability of contact between the necessary species. Physically, the sintering rate (M_g) represents the rate iron and silicates are brought to the interface of particles in contact to mix. This rate is based on an effective diffusion coefficient (Equation

$$\frac{d(G)}{dt} = M_g X_g \quad (10)$$

Figure 5.3.1 Ash Sintering During Combustion

$$D_g = \left(\frac{\gamma}{\mu} \right) L \quad (11)$$

11) as proposed by Nowak et al. (1990). This diffusion coefficient is given by the melt viscosity (μ), surface tension (γ), and the mean jump length of atoms or clusters in the melt (L , assumed to be constant). It was further shown by Nowak et al. that the ratio ($\gamma L/\mu$) fits an Arrhenius-type equation (Equation 12). The activation coefficient (E_g/k) was found to have a range of 2000-35000 K⁻¹ from ash data from

$$D_g = D_{g0} \exp\left(\frac{-E_g}{kT_p}\right) \quad (12)$$

several coals under different conditions (Nowak, 1990). A value of 12573 K⁻¹ was chosen for this work as it represents the temperature dependence of iron diffusing in silicate melts (Turkdogan, 1983). This temperature dependence is also in the range from Nowak. The effective sintering rate constant K_g was then given by Equation 13. Unfortunately, data is not available to explicitly determine many of the

$$K_g = \frac{D_{g0} \rho_{sil} \exp\left(\frac{-E_g}{R T_p}\right)}{r_{sil}} \quad (13)$$

necessary parameters in Equation 13, so the unknown parameters were lumped into the fit parameter G_k , Equation 14. Finally, the overall sintering rate M_g was given by Equation 15, where SA_{sil} is defined by Equation 16.

$$G_k = \frac{D_{g0} \rho_{sil}}{r_{sil}} \quad (14)$$

$$M_g = G_k \exp\left(\frac{-E_g}{RT_p}\right) SA_{sil} \quad (15)$$

$$SA_{sil} = (Sil) \frac{3}{r_{sil} \rho_{sil}} \quad (16)$$

The next major component of the glass formation rate is the probability that silicate species contact iron species as opposed to any other species (including itself). This probability, X_g (Equation 17), is defined as the cross-sectional area of molten iron

$$X_g = \frac{CSA_{molten}}{\max\{SA_{char}, CSA_{ash}\} - CSA_{molten}} \quad (17)$$

on the surface (CSA_{molten}) divided by the surface area not occupied by molten iron species (either open char or area occupied by other species). CSA_{molten} and CSA_{ash} are defined in Equations 18 and 19 respectively. Due to the lack of size change with time (agglomeration) data, these Equations are based on the mass mean size of the minerals in the original coal. The iron oxide is also assumed to maintain the same size and density of the original pyrite. The glass particle density and size are

$$CSA_{molten} = [(Fe_{0.877}S) + (Fe_3O_4)_{molten}] \frac{3}{4 r_{pyr} \rho_{pyr}} \quad (18)$$

$$CSA_{ash} = CSA_{molten} + (Sil) \frac{3}{4 r_{sil} \rho_{sil}} + (G) \frac{3}{4 r_{glass} \rho_{glass}} \quad (19)$$

estimated by a mass weighted average of the silicate and pyrrhotite sizes and densities (based on the parameter y , Section 5.2).

In order for the assumed form of X_g (Equation 17) to be valid, the total cross-sectional area of molten species must always be much greater than the total cross-sectional area of ash on the surface. Figure 5.3.2 shows the typical behavior of SA_{char} , CSA_{ash} , and CSA_{molten} with time. As can be seen from the figure, SA_{char} is initially much larger than CSA_{ash} . However, eventually CSA_{ash} becomes larger than SA_{char} . At this point CSA_{ash} becomes more important in determining the probability of contact. It is important to note that either SA_{char} or CSA_{ash} are always greater than CSA_{molten} . Therefore, the assumed form of X_g is reasonable.

An interesting property of X_g is its behavior during char burnout. Figure 5.3.3 illustrates the general (ideal) behavior as a function of time during burnout. As previously mentioned, SA_{char} at the beginning of combustion ((a) on Figure 5.3.3) is much larger than CSA_{ash} and CSA_{molten} . The probability of contact, then, is fairly low as the particles on the surface are separated by open char spaces. As combustion progresses the char recedes and exposes more iron and silicate species ((b) on Figure 5.3.3). As very little glass formation and pyrrhotite oxidation has taken place by this point, most of the material on the surface is molten iron species and silicates. Therefore the probability of contact is very high. Finally, as the char continues to recede and more of the available surface area is occupied by other

Figure 5.3.2 Behavior of SA_{char} , CSA_{molten} , and CSA_{ash} (Run 27; Kent. No. 11)

Figure 5.3.3 Behavior of Contact Probability During Burnout; (a) large amounts of open char area, (b) smaller char surface, primarily silicates and molten iron species on surface, (c) glass and solid iron oxide impede contact

Figure 5.3.4 Behavior of Contact Probability During Model Simulations

species (glass and solid oxide) contact between the necessary species is impeded and X_g decreases ((c) on Figure 5.3.3).

Although the behavior of X_g follows the same general path as described above, there are some interesting points about the behavior under 'real' conditions. Figure 5.3.4 shows how X_g varies with time for experiments from two coals. In Run 67 (Kentucky No. 9) the 'observed' (calculated during the simulation) behavior closely matches the ideal behavior. The simulation for Run 27 (Kentucky No. 11) also initially follows the ideal trend. However, when the char temperature exceeds 1600K, X_g increases dramatically. This increase is due to the availability of molten iron oxide for capture (Section 5.2). X_g then becomes relatively constant. During this time the consumption of the molten iron species (by glass formation) is balanced by the rate molten iron species are exposed. Finally, the presence of larger amounts of glass, combined with a char temperature less than 1600 K, causes X_g to decrease during the final stages of burnout.

The mass of silicates on the surface, as discussed above, is a very important parameter. The surface of the char is, again, treated as a batch reactor with an input stream (Equation 20). The mass of silicates that have come into the 'reactor' is given by the amount of char consumed and the mass fraction silicates in the char. The mass of silicates removed from the 'reactor' is given by the amount of glass that has been formed and the mass fraction silicates in the glass (Section 5.2).

$$(Sil) = \{(CHAR)_0 - (CHAR)\} MF_{sil} - (G) \left(\frac{y}{y+1} \right) \quad (20)$$

In addition, as the proposed glass formation mechanism is based on mixing of molten species, the silicate mass on the surface is set to zero for temperatures less than the silicate melting temperatures. Although the melting points of pure mineral species is often very high, addition of small amounts of impurities dramatically decreases the melting points of a mineral. It was noted by Scotto (1992) in a related study that of the kaolinite injected into the furnace (the same furnace as used in this work) approximately ½ of the particles melted at furnace temperatures much lower than the pure species melting temperature (2083 K). These kaolinite particles have a similar composition as those found in the study coals. Further evidence for the lower melting points was found as part of this work. Throughout the EDX-SEM portion of this work (and the Auger portion of the work by Gallagher, 1992) all of the observed ash particles were spherical, suggesting melting had occurred during the combustion process.

In order to estimate the effect of impurities on the melting points, the mineral compositions given from CCSEM (see Section 3.2) were normalized to an SiO₂-Al₂O₃-K₂O (the K₂O represents both the K₂O and the Na₂O fraction in the coal) system. The solidus temperature, the temperature where the first liquid appears for a given system, was then determined from equilibrium diagrams (*Slag Atlas*, 1989) for the calculated compositions. The solidus temperatures for the non-quartz species

were similar for all the coal compositions (Table 5.3.1). For the quartz fraction, the temperature was much higher, but not as high as the melting point of pure SiO_2 (1983 K).

Table 5.3.1. Silicate Melting Temperatures (Slag Atlas, 1981)

Silicate (Pure Species Composition, Raask, 1985)	Melting Temperature (K)
Illite (K_2O $3\text{Al}_2\text{O}_3$ 6SiO_2 $2\text{H}_2\text{O}$ + Fe, Ca)	1258
Kaolinite (Al_2O_3 2SiO_2 $2\text{H}_2\text{O}$)	1258
"Mixed" (varied, see Chapter 3)	1258
Quartz (SiO_2)	1650

5.4 Char Burnout

As can be seen from the previous sections, the char burnout rate is an extremely important part of the partitioning model. The amount of material on the surface of the char, the local and bulk oxygen partial pressure, and the char temperature all depend on the char burnout rate. The char burnout relation used here, Equation 21, was that presented by Hurt and Mitchell (1992). According to this empirical study, the global char burnout rate is a function of the char external surface area (SA_{char})

$$\frac{d(CHAR)}{dt} = -K_c \exp\left(\frac{-E_c}{RT_p}\right) SA_{char} (P_{O_{2s}})^{1/2} \quad (21)$$

and the char particle temperature (T_p). The burnout rate was assumed to be proportional to the square root of the surface oxygen partial pressure ($P_{O_{2s}}$). Finally, the global rate constants were determined empirically (by fitting to data from several coals) to be a function of the coal carbon content (%C, ash and H_2O free) as shown in Equations 22 and 23 (Hurt et al, 1992), where $T_{ref}=1750$ K.

$$E_c = -5.945 + 0.355(\%C) \quad (22)$$

$$\ln K_c = (2.80 + 0.0758(\%C)) - \left(\frac{E_c}{T_{ref} R} \right) \quad (23)$$

It should be noted that Hurt et al. (1992) found that the lower rank coals burned in

the diffusion limited regime. This fact was taken into account during the derivation of the parameters in Equations 22 and 23. Therefore, the model allows the lower rank coals (Beulah Lignite and Eagle Butte) to burn much faster than the bituminous coals. It was further assumed that the coals do not swell appreciably and shrink (with constant density) as the carbon is burned away. This is consistent with the findings of Smith (1971) for bituminous coals

In the model the combustion product is assumed to be CO. The CO is then oxidized to CO₂ in the bulk gas phase according to equation 24. The global forward and

reverse reaction rates, R_f and R_b , shown in Equations 25 and 26, are those presented by Dryer et al (1973) and Westbrook et al (1981) respectively. The species

$$R_f = 3.8 \times 10^{14} V_g \exp\left(\frac{-E_{CO}}{R T_g}\right) [CO] [H_2O]^{1/4} [O_2]^{1/2} \quad (25)$$

$$R_b = 1 \times 10^{11} V_g \exp\left(\frac{-E_{CO}}{R T_g}\right) [CO_2] \quad (26)$$

concentrations are determined from the number of moles of each species in the system and the gas volume (from Equation 27). Mole balances for O₂, CO, CO₂ are shown in Equations 28 through 30. Finally, the surface partial pressure of oxygen is determined by assuming a steady state between oxygen transport and consumption

(see Equation 31).

$$V_g = \frac{n_t R T_g}{p} \quad (27)$$

$$\frac{d\{O_2\}}{dt} = \frac{1}{24} \frac{d(CHAR)}{dt} + \frac{1}{2}(R_b - R_f) \quad (28)$$

$$\frac{d\{CO\}}{dt} = -\frac{1}{12} \frac{d(CHAR)}{dt} + (R_b - R_f) \quad (29)$$

$$\frac{d\{CO_2\}}{dt} = R_f - R_b \quad (30)$$

$$\left(\frac{D}{r_c}\right) \left(\frac{P_{O_2} - P_{O_{2s}}}{R T_g}\right) = \frac{-k_c}{24} \exp\left(\frac{-E_c}{R T_p}\right) (P_{O_{2s}})^{1/2} \quad (31)$$

As there is no simple means to take into account the coal devolatilization it is assumed that devolatilization has taken place before the char begins to burn. The initial amounts of each of the gaseous species are determined from the coal mass, the stoichiometric ratio, and the fraction of volatile matter.

5.5 Particle Energy Balances

All of the relations discussed to this point have been strongly dependent on the char particle temperature and the extraneous pyrite temperature. In order to determine these temperatures, energy balances were performed on the char (Equation 32) and the extraneous pyrite (Equation 33). Each energy balance consisted of a conduction term, a radiation term, and a reaction term.

$$\frac{dT_p}{dt} = \frac{SA_{char}(h_c(T_g - T_p) + \sigma \epsilon (T_w^4 - T_p^4)) + \frac{d(CHAR)}{dt} \Delta H_c}{C_p(CHAR)} \quad (32)$$

$$\frac{dT_{pyr}}{dt} = \frac{SA_{extpyr}(h_p(T_g - T_{pyr}) + \sigma \epsilon (T_w^4 - T_{pyr}^4)) + \frac{d(Fe_3O_4)}{dt} \Delta H_r}{C_{p_{pyr}}(Fe_{0.877S})_{ext}} \quad (33)$$

The first component of each energy balance, the conduction term, utilized a heat transfer coefficient (h) based on the mean film temperature (to determine thermal conductivity) and the particle diameter. The radiation term utilized a particle emissivity of 0.8 for the char and 0.5 for the extraneous pyrite (Gallagher, 1992, Srinivasachar, 1989) and a wall temperature (T_w) of 98% of the gas temperature. The gas temperature measured experimentally was fitted to Equation 34. This form

$$T_g = a_1 \exp(-a_2(a_3+t)) (1 - \exp(-a_4(-a_2(a_3+t)))) + a_5 \quad (34)$$

was chosen simply because it best fit the data. The final energy term for the char energy balance, heat of combustion of the char was calculated from Equation 35

$$\Delta H_c = \frac{25428 + 0.82T_p + 0.0003T_p^2 + \frac{213000}{T_p}}{12} \quad (35)$$

$$C_p = \frac{4.03 + 0.00114T_p - \frac{204000}{T_p^2}}{12} \quad (36)$$

(Gallagher, 1992) based on the assumption that CO is the primary reaction product. The bulk char heat capacity was calculated from Equation 36 (Gallagher, 1992). For the extraneous pyrite the heat of reaction was dependent on the state of the pyrrhotite ($\Delta H_r = -201.24 \text{ kJ mole}^{-1} \text{ O}_2$ for solid pyrrhotite, $-190.10 \text{ kJ mole}^{-1} \text{ O}_2$ for liquid pyrrhotite, Srinivasachar, 1989).

These relations gave particle temperatures consistent with those found in the literature. For example, the team of Hurt and Mitchell (1992) measured peak particle temperatures as part of their combustion rate study (Section 5.5). These temperatures were generally 100-300 °K above the peak gas temperatures, depending on the combustion conditions and coal type. The calculated pyrrhotite temperatures (approximately 1500-1700 K) were also consistent with those found for oxidizing pyrite particles under lower P_{O_2} conditions (Asaki et al., 1985, Jorgenson, 1981). Typical calculated particle temperature profiles for several coals can be seen in

Figures 5.5.1 through 5.5.4. In general the char temperatures mirror the gas temperatures. The particle temperature overshoot is due to film heat transfer resistance.

Figure 5.5.1 Temperature Profiles for Run 67; Kentucky No. 9 (SR=1.2)

Figure 5.5.2 Temperature Profiles for Run 61; Eagle Butte (SR=1.2)

Figure 5.5.3 Temperature Profiles for Run 73B; Kentucky No. 11 (SR=0.79)

Figure 5.5.4 Temperature Profiles for Run 22; Beulah Lignite (SR=1.2)

5.6 Model Parameters and Assumptions

Although most of the model input parameter, fit parameters, and assumptions have been introduced in previous sections, they are summarized in the following tables:

Table 5.6.1 Model Input Parameters

Parameter	Source
g inherent silicate/g coal g inherent pyrite/g coal g extraneous pyrite/g coal	Calculated from Mass Fraction of Each Species in Coal (CCSEM of Coal, Univ. Kentucky) and Mass Fraction Inherent of Each Species (CCSEM of Ash, Univ. of Kentucky)
Mass Distribution of Silicate Species	Measured by CCSEM of Coal (Univ. of Kentucky)
Mass Mean Char Size	Measured (by PSI)
wt% Volatiles in Coal wt% Ash in Coal wt% Moisture in Coal wt% H in Coal wt% C in Coal	Measured (by Foster Wheeler Development Corp.)
Mass Mean Size Silicates and Pyrite	Estimated from Mass Fraction Inherent for Each Species and Mass-Size Distribution of Each Species in Coal (CCSEM)
Mass Fraction of Original Iron in Clays	Measured by Mössbauer (Univ. Kentucky)
Stoichiometric Ratio Gas Temperature Profile	Measured as Part of Experimental Procedure

Table 5.6.2 Fitted Model Parameters

Parameter	Physical Significance
G_k	Sintering Rate Constant; Related to Several Melt Properties Not Available in Literature
y	Average Amount of Silicate Consumed During Glass Formation, Can't Use Coal Properties (eg; Inherent Silicon to Iron Ratio) as Some Coals May Have an Excess of Silicates or Iron for Glass Formation

Table 5.6.3 Model Assumptions

Assumption	
No Coagulation of Extraneous Pyrites, Silicates, or Char	Particles Fall At Approximately Flue Gas Velocity, Particles Relatively Large
No Iron Fume Formation	No Experimental Evidence to Support Iron Fume Formation (Section 4.2)
No Pyrite Fragmentation	No data available, Inherent Pyrite May Fragment Inside Char but Will Coalesce When Pyrrhotite Melting Occurs
Viscous Sintering	Solid-Solid Sintering Generally Much Slower than Viscous Sintering, Generally Have Molten Materials Through Most of Burnout (from Model)
Silicate Melting Temperatures Lower than "Pure" Species Melting Temperatures	Impurities Measured in Mineral Species (Section 3.3), Scotto (1992) and Raask (1985) showed Evidence of Silicate Melting at Lower Temperatures when Impurities Present, EDX-SEM and Auger Sections of this Work Found only Spherical Ash Particles
Probability of Inherent Iron-Silicate Contact Given by Species Crosssectional Areas (Equation 17)	Cross-Sectional Areas of Molten Iron Species are Always Much Less Than Surface Area of Char or Cross-Sectional Area of Ash (Section 5.3)

5.7 Model Validation

In order to determine the validity of the proposed model, several simulations were performed to predict the partitioning of iron into phases measurable by Mössbauer analysis. From this partitioning it was possible to estimate the fraction of iron in slag causing phases (ϕ ; glass, molten iron species) at any time in the combustion process. These simulations utilized the experimental input parameters from several experiments with a number of coals. These parameters, seen in Table 5.7.1, include the peak gas temperature (and the gas temperature profile), the coal composition, and the stoichiometric ratio. The simulations, performed to mirror the experiments, include temperature variations, coal composition variations, and stoichiometric ratio variations. The previously mentioned fit parameters, G_k and y , were determined by a multivariable fitting routine to have values of approximately $10112.5 \text{ (g glass s}^{-1} \text{ cm}^{-2})$ and 8.1 respectively.

A comparison of the predicted versus measured (by Mössbauer) partitioning of iron into the slag causing phases present at the end of combustion (primarily pyrrhotite and glass), Figure 5.7.1, shows that the model agrees reasonably well with the data. This fit is especially good for the superstoichiometric cases, but fails slightly at the lower stoichiometries and particle temperatures. This behavior may be due to the use of the liquid/solid mass transfer coefficient derived by Srinivasachar et al. (1989). The coefficients, described in Section 5.2, were used by Srinivasachar et al as a fit

parameter to fit the data from Jorgenson (1981). This data was all obtained under oxidizing conditions. Further, the solid mass transfer coefficient was fit as a function of the gas mass transfer coefficients. This fit may obscure important liquid mass transfer phenomena, including the temperature and size dependence. This aspect of the model, as also pointed out by Srinivasachar et al., needs to be explored further, preferably in a smaller scale combustor.

Table 5.7.1 Experimental Parameters

Run	Coal	Feedrate (kg/hour)	Stoichiometric Ratio	Peak Gas Temp (K)
21	Illinois #6	1.7	1.27	1635
47b		1.3	1.30	1577
47h		2.3	1.24	1641
70b		3.5	1.19	1718
70c		3.5	1.19	1718
67	Kentucky #9	1.7	1.30	1539
68		2.3	1.20	1475
69a		3.2	1.21	1633
69c		3.2	1.21	1633
27	Kentucky #11	1.7	1.25	1593
56c		1.3	1.25	1513
56f		2.1	1.20	1702
57		1.8	0.80	1390
58		1.8	1.32	1713
72		2.8	0.72	1693
73b		2.5	0.79	1574
73e		2.5	1.00	1619
74c		1.7	0.79	1418
74e		1.7	0.90	1428
22	Beulah Lignite	2.4	1.32	1567
48b		1.6	1.26	1493
48f		2.6	1.37	1518

Table 5.7.1 Experimental Parameters (cont'd)

Run	Coal	Feedrate (kg/hour)	Stoichiometric Ratio	Peak Gas Temperature
32	Upper Freeport	1.7	1.23	1620
35		1.7	1.30	1573
71		3.6	1.19	1684
23	Eagle Butte	2.3	1.26	1493
61		2.1	1.33	1466
64		2.3	1.33	1429

Table 5.7.2 Simulation Results

Run	Coal	ϕ (meas.)	ϕ (pred.)	Peak Char Temp. (K)	Peak Pyrite Temp. (K)
21	Illinois #6	0.160	0.196	1674	1663
47b		0.180	0.195	1650	1642
47h		0.320	0.196	1686	1677
70b		0.256	0.186	1798	1753
70c		0.259	0.186	1798	1753
67	Kentucky #9	0.233	0.227	1583	1579
68		0.255	0.221	1539	1543
69a		0.345	0.461	1664	1637
69c		0.384	0.461	1664	1637
27	Kentucky #11	0.260	0.332	1641	1614
56c		0.230	0.311	1577	1563
56f		0.336	0.330	1747	1703
57		0.450	0.604	1401	1388
58		0.390	0.332	1769	1733
72		0.764	0.855	2030	1833
73b		0.660	0.626	1540	1524
73e		0.360	0.332	1615	1590
74c		0.694	0.544	1581	1325
74e		0.458	0.420	1403	1349
22	Beulah Lignite	0.280	0.310	1564	1537
48b		0.370	0.310	1517	1496
48f		0.380	0.310	1608	1535

Table 5.7.2 Simulation Results (cont'd)

Run	Coal	ϕ (meas.)	ϕ (pred.)	Peak Char Temp. (K)	Peak Pyrite Temp. (K)
32	Upper Freeport	0.300	0.508	1676	1675
35		0.400	0.433	1589	1623
71		0.486	0.508	1777	1753
23	Eagle Butte	0.540	0.462	1600	1554
61		0.727	0.617	1627	1561
64		0.812	0.727	1718	1654

Table 5.7.3 Calculated Burnout and Sample Residence Times

Run	Coal	Calculated Burnout Time (sec)	Calculated Residence Time, Port 11 (sec)
21	Illinois #6	0.583	3.49
47b		0.600	3.49
47h		0.559	2.88
70b		0.400	1.86
70c		0.400	1.86
67	Kentucky #9	0.801	3.43
68		1.187	3.31
69a		0.675	2.25
69c		0.675	2.25
27	Kentucky #11	0.694	3.83
56c		0.786	5.07
56f		0.483	2.83
57		IC	4.18
58		0.474	3.91
72		IC	4.05
73b		IC	4.35
73e		1.263	3.84
74c		IC	7.55
74e		IC	6.31
22	Beulah Lignite	0.766	4.06
48b		0.865	6.05
48f		0.590	3.40

IC = Incomplete Combustion

Table 5.7.3 Calculated Burnout and Sample Residence Times (cont'd)

Run	Coal	Calculated Char Burnout Times (sec)	Calculated Residence Time, Port 11 (sec)
32	Upper Freeport	0.921	3.88
35		1.470	3.88
71		0.722	1.74
23	Eagle Butte	0.727	3.60
61		0.642	3.60
64		0.532	3.48

Figure 5.7.1. Comparison of Predicted and Measured Fraction Iron as Glass and Pyrrhotite

Section 5.8: Effect of Combustion Conditions and Ash Composition on Partitioning

Although the model developed in the previous sections adequately describes the partitioning of iron during combustion, it requires knowledge of several characteristic parameters. Unfortunately, due to the detailed ash and coal analysis need to determine these parameters, they are not always readily available for coals of interest. Therefore the model, in conjunction with experimental results, were used to qualitatively describe the partitioning of iron in fly ash as a function of several important variables. These variables include the peak char temperature, the iron and silicate distribution, and the stoichiometric ratio.

The effect of the peak char temperature, seen in Figure 5.8.1, is fairly small, suggesting that pyrrhotite is the major iron species captured into the glassy phase. The primary temperature effect occurs around 1600 K. Those coals that have data around this temperature exhibit a slight increase in iron capture when char temperatures exceed 1600 K. This effect can be attributed to the solidification of iron oxide melts at temperatures less than 1600 K (see Section 5.2). Therefore, at temperatures greater than 1600 K there are more iron species available for capture into the glass phase. Data for some coals, specifically the Eagle Butte and Kentucky No. 11, suggest an additional increase in iron capture with temperature. However, in general the additional increase in capture is minimal.

Figure 5.8.1 Effect of Temperature on Iron Partitioning

Another important parameter for iron partitioning is the ash composition and its distribution through the coal. The fraction of pyrite as extraneous pyrite, for example, has a large effect on the overall iron captured in the glassy phase. This effect is due to the fact that the extraneous pyrite does not interact with extraneous silicates or with the char (see Section 5.1). Therefore, the larger the fraction of extraneous pyrite, the lower the pyrite fraction available for glass capture. This does not say, however, that the extraneous pyrites are not a problem. Rather, it says that the ash obtained at the end of the combustion process will be lower in iron as glass. Therefore, for superstoichiometric conditions, the final ash will be less sticky (Abbot and Austin, 1985, etc., see Chapter 1). The effect of extraneous pyrites on potential slagging, as predicted from this work, will be discussed in the next section.

The next major coal composition effect is the mass of inherent silicates relative to the mass of inherent pyrite. As the relative amount of silicates increases, the possibility that inherent pyrites can oxidized and solidify (under the appropriate conditions) before coming in contact with the silicates decreases. Therefore, the amount of iron in the glass phase should increase with the following parameter:

$$P_{Si/Fe} = \left(\frac{\frac{g \text{ silicate}}{g \text{ coal}}}{\frac{g \text{ pyrite}}{g \text{ coal}}} \right)_{inh} \left(\frac{\frac{g \text{ pyrite}_{extr.}}{g \text{ coal}}}{\frac{g \text{ pyrite}}{g \text{ coal}}} \right)$$

Note that the mass fraction pyrite as extraneous pyrite was included to take into account the previously mentioned effect of extraneous pyrite. Figure 5.8.2 shows that the iron capture does, in fact, increase with this parameter. The only coal that varies slightly from this trend, the Upper Freeport, contains a significant fraction of iron as silicate in the original mineral matter.

The final parameter under consideration is the effect of stoichiometric ratio on iron partitioning. For superstoichiometric conditions the primary iron containing slag contributor in the fly ash is iron glass. This assumes that all available pyrite is either oxidized or captured. As the stoichiometric ratio is decreased, however, significant pyrrhotite can remain in the fly ash. In general the iron fraction in the glass and/or pyrrhotite phases increases dramatically with decreasing stoichiometric ratio (Figure 5.8.3). This increase is due primarily to the increase in unoxidized pyrites (as pyrrhotite). The iron fraction as glass, Figure 5.8.4, is relatively constant with stoichiometric ratio.

In general, the iron fraction in slag contributing phases, glass and/or pyrrhotite, increases if char temperatures exceed 1600 K. This fraction also increases (under superstoichiometric conditions) with the ratio $(\text{mass silicates}/\text{mass pyrite})_{\text{inh}}$ multiplied by the fraction of pyrite as extraneous pyrite. Finally, decreasing the stoichiometric ratio causes more pyrrhotite to remain in the fly ash, creating a net increase in the iron fraction in slag contributing phases.

Figure 5.8.2 Effect of Silicon/Pyrite Ratio in Coal

Figure 5.8.3 Effect of Stoichiometric Ratio on Fraction Iron as Glass and Pyrrhotite

Figure 5.8.4 Effect of Stoichiometric Ratio on Fraction Iron as Glass

Section 5.9 Practical Applications of Model

The first part of exploring the practical applications of a model is a comparison of model derived predictions with predictive techniques currently used in practice. Although many empirical indices have been proposed to predict slagging and fouling propensities, only a few "typical" indices will be discussed here (primarily those discussed by Raask, 1985).

Before looking at the various predictions, it is important to note that many other factors not investigated as part of this work (alkali and calcium content, for example) have been implicated as major factors in enhancing slagging and fouling. For this reason, only results for the high iron (bituminous) ashes will be compared to empirical slagging and fouling indices.

The first set of empirical indices are those developed by Raask (1985) for high iron British coals. The fraction of iron, as Fe_2O_3 , in the ash is the first such parameter. In general, the higher the iron content, the higher the slagging propensity (Table 5.9.1). The silica ratio, developed by Reid and Cohen (1944), is another index used by Raask to evaluate high iron content coals. This index is defined by Equation 37,

$$\text{Silica Ratio} = \frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}} \quad (37)$$

where SiO_2 , etc., is the mass fraction of that species in the ash. The higher the silica ratio, the lower the slagging propensity (probably due to an increase in melting temperatures and melt viscosities). The various slagging classifications can be seen in Table 5.9.1.

Another major slagging index was developed by Gray and Moore (1974) based on the deformation temperatures determined in ash fusion tests. The index, F_s , is given by Equation 38. IT is the initial deformation temperature, and HT is the hemisphere

$$F_s = \frac{4 \text{ IT} + \text{HT}}{5} \quad (38)$$

temperature. Slagging classifications for this parameter are given in Table 5.9.2.

The final slagging index considered here is the ratio of basic to acidic oxides in the ash (as based on slag bonding, see Chapter 1). This index is given by Equation 39,

$$R_{b/a} = \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2} \quad (39)$$

where the species are given as weight percent of the ash. The critical value for this parameter has been determined as 0.55 by Duzy (1965) and by Duzy and Walker (1965). At this value the ash fusion temperature is at its minimum (thus fouling and slagging is at a maximum). Raask (1985) mentions a maximum value of 0.50 for pulverized coal fired boilers.

Table 5.9.1 Slagging Classifications (Raask, 1985)

Slagging Index	No Slagging	Some Slagging	High Slagging
Weight % Iron Oxide in Ash	3-8	8-15	15-23
Silica Ratio	72-80	65-72	50-65

Table 5.9.2 Slagging Classifications Based on F_s (Raask, 1985)

Slagging Index (F_s , K)	Slagging Classification
1505-1615	Medium
1325-1505	High
<1325	Severe

In order to compare model predictions for the bituminous coals in this study with the empirical slag indices, it is necessary to define a new parameter to take into account both slagging and fouling. It is well known that the extraneous pyrite is a major slagging contributor, therefore a good measure of the slagging and fouling propensity of the ash is given by the fraction of iron in the glassy phase (assumed to be sticky) and the fraction of iron originally as extraneous pyrite. Thus the model results, in conjunction with coal mineral matter information, can be used to predict the slagging and fouling propensities for high iron coals. The empirical predictions for the study coals, and the newly defined parameter can be seen in Table 5.9.3.

Table 5.9.3 Slag Indices and Model Predictions for Bituminous Study Coals

Coal	Slag Index				
	Wt.% Fe_2O_3 in Ash	Silica Ratio	$R_{b/a}$ (base/acid ratio)	F_s (Temperature, K)	Model Prediction
Ill. No. 6	20.5: High Slag	64: High Slag	0.46	1500: High Slag	0.63
Kent. No. 11	20.2: High Slag	65: High Slag	0.45	1540: High Slag	0.57
Kent. No. 9	22.4: High Slag	63: High Slag	0.46	1517: High Slag	0.60
Up. Free.	13.5: Some Slag	75: No Slag	0.27	1606: Low Slag	0.54

From these results we can see that three of the study coals, Illinois No. 6, Kentucky No. 11, and Kentucky No. 9, are predicted to be medium to high slaggers. This corresponds well with the model prediction that approximately half of the iron is in slagging and fouling enhancing phases. The only coal where model predictions do not correspond to the empirical indices is the Upper Freeport. This coal, according to the model predictions, should be a high slagging coal. However, the empirical indices predict a fairly low slagging propensity for this coal. Unfortunately, quantitative data is not available to determine which of the predictions are in error. However, the discrepancy for the Upper Freeport may be due to the fact that this coal has the lowest iron content of the bituminous coals. This topic will be addressed in the future work section (Chapter 6)

Much of the driving force for developing this partitioning model has been the assumption that the amount of iron captured in the glassy phase has a large effect on the stickiness of the resulting ash. Although other factors may influence ash stickiness, it is important to compare the fraction of iron captured and the stickiness of the ash. Early in this project researchers at PSI evaluated the stickiness of fly ash from the coals in this study under various conditions. The results of this study can be seen in Figure 5.9.1. In Figure 5.9.2 the coals used in this part of the overall project were ranked according to the fraction of iron in the glassy phase. A comparison of the two figures shows (with the exception of the Upper Freeport) a

Figure 5.9.1 Collection Efficiency (adhesion) from Boni et al. (1990)

Figure 5.9.2 Fraction of Iron as Glass for Study Coals

fairly good qualitative correlation between the fraction iron as glass and the ash stickiness. This is especially true if the Eagle Butte is ranked higher for stickiness than the Beulah Lignite (Figure 5.9.1 suggests may be the case).

This partitioning model has one unique practical application. This model allows a design engineer to predict where the critical slagging and fouling points are for a given coal under certain conditions. For example, if an engineer knows (or can estimate) the coal time-temperature history, he can determine how the iron is partitioned as a function of residence time. This information can then be used to predict areas in the furnace where slagging and fouling may occur. In order to clarify this process, simulations for different study coals under varied conditions were performed (Figures 5.9.3 through 5.9.6). In the superstoichiometric simulations (Figures 5.9.3 through 5.9.5) the first critical slagging point occurs at 0.40, 0.20, and 0.23 sec. respectively. This represents the time when the extraneous pyrrhotite has reached its melting point (creating a sticky molten phase). The second critical point for these three experiments occurs when char burnout is complete. In most cases (Figures 5.9.4 and 5.9.5) all of the pyrrhotite has either oxidized or been captured into glass by this point. Therefore the slagging propensity remains reasonably constant until the particle temperature drops below the melting point of the glassy phase. However, in the case of the Beulah Lignite, Figure 5.9.3, the char burnout kinetics are very fast. The char burns away and exposes the inherent mineral matter faster than the pyrrhotite can oxidize or be captured. In this case the slagging

Figure 5.9.3 Partitioning of Iron as a Function of Time, Run 22; Beulah Lignite

Figure 5.9.4 Iron Partitioning as a Function of Time, Run 61; Eagle Butte

Figure 5.9.5 Iron Partitioning as a Function of Time, Run 67; Kentucky No. 9

Figure 5.9.6 Iron Partitioning as a Function of Time, Run 73B; Kentucky No. 11

propensity decreases slightly as some of the remaining pyrrhotite oxidizes.

For substoichiometric conditions, Figure 5.9.6, the iron partitioning becomes more interesting. In this case, although the first critical point occurs at approximately 0.25 sec., appreciable molten pyrrhotite remains through out the process. This pyrrhotite is molten until the mixture drops below the crystallization temperature of the melt (taken as 1356 K in this case). The same process is true for the inherent mineral matter. The exposed mineral matter contains a large fraction of unoxidized pyrrhotite and glass. Therefore the second critical area begins at approximately 0.6 sec. and continues until both the glass and the molten pyrrhotite solidify at approximately 1.0 and 1.2 sec respectively.

In conclusion, the model developed as part of this work is consistent, for high iron content coals, with the slagging and fouling indices currently used in practice. This model can also be used to qualitatively predict the adhesiveness of fly ash from various coals. Finally, and probably most importantly, this model provides a unique method for predicting problem areas during combustion.

5.10 Glossary of Model Variables

Variable	Definition
a_1 - a_5	Fit Parameters of Gas Temperature Profile
(CHAR)	Mass of Char (g)
(CHAR) ₀	Initial Mass of Char (g)
$C_{\text{mol-mass}}$	Conversion Factor (g Fe ₃ O ₄ mole O ₂ ⁻¹)
C_p	Mean Char Heat Capacity (cal g ⁻¹ K ⁻¹)
$C_{p \text{ pyr}}$	Pyrite Heat Capacity (cal g ⁻¹ K ⁻¹)
{CO}	Moles of CO in System
[CO]	Concentration CO (mole cm ⁻³)
{CO ₂ }	Moles CO ₂ in System
[CO ₂]	Concentration CO ₂ (mole cm ⁻³)
CSA _{ash}	Tot. Cross-Sect. Area Ash (cm ²)
CSA _{molten}	Tot. Cross-Sect. Area Molten Fe Compounds (cm ²)
D	Gas Phase Diffusivity (cm ² s ⁻¹)
D_g	Sintering Effective Diffusivity (cm ² s ⁻¹)
D_{g0}	Preexponential Effective Diff. Constant (cm ² s ⁻¹)
E_c	Char Oxidation Activation Energy (kcal mole ⁻¹)
E_{CO}	CO Oxidation Activation Energy (kcal mole ⁻¹)
E_g/k	Effective Diffusivity Temp. Dependence (°K ⁻¹)
E_p	Iron Oxidation Activation Energy (kJ mole ⁻¹)
(Fe ₃ O ₄)	Mass Fe ₃ O ₄ on Char Surface (g)
(Fe ₃ O ₄) _{molten}	Mass Molten Fe ₃ O ₄ on Char Surface (g)
(Fe _{0.877} S)	Mass Fe _{0.877} S on Char Surface (g)
(Fe _{0.877} S) _{ext}	Mass of Extraneous Fe _{0.877} S Particle (g)
(G)	Mass Glass on Char Surface (g)

Model Variable Definitions (cont'd)

Variable	Definition
G_k	Fitted Sintering Rate Constant ($\text{gG s}^{-1} \text{cm}^{-2}$)
$[\text{H}_2\text{O}]$	Concentration Water (mole cm^{-3})
h_c	Char Heat Transfer Coeff. ($\text{cal cm}^{-2} \text{K}^{-1} \text{s}^{-1}$)
h_p	Pyrite Heat Transfer Coeff. ($\text{cal cm}^{-2} \text{K}^{-1} \text{s}^{-1}$)
K_c	Char Oxidation Rate Constant ($\text{gC s}^{-1} \text{cm}^{-2} \text{atm}^{-1/2}$)
K_g	Sintering Rate Constant ($\text{gG s}^{-1} \text{cm}^{-2}$)
k_m	Gas Phase Mass Transfer Coefficient (cm s^{-1})
k_l	Liquid Phase Mass Transfer Coefficient (cm s^{-1})
k_o	Overall Mass Transfer Coefficient (cm s^{-1})
K_p	Iron Oxidation Rate Constant (cm s^{-1})
K_{p0}	Preexponential Iron Oxidation Rate Constant (cm s^{-1})
L	Mean Atom Jump Length During Sintering (cm)
M_g	Silicate-Iron Sintering Rate (g sec^{-1})
MF_{pyr}	Mass Inherent Pyrite in Char (g gchar^{-1})
MF_{sil}	Mass Inherent Silicate in Char (g gchar^{-1})
n_t	Total Number Gaseous Moles in System
$\{\text{O}_2\}$	Moles O_2 in System
$[\text{O}_2]$	Concentration O_2 (mole cm^{-3})
P_{O_2}	Oxygen Partial Pressure in Bulk Phase (atm)
$P_{\text{O}_{2s}}$	Oxygen Partial Pressure on Surface (atm)
P	Total System Pressure (atm)
R	Gas Constant
R_b	Rate of CO_2 Reduction (mole s^{-1})

Model Variable Definitions (cont'd)

Variable	Definition
r_c	Radius of Char (cm)
r_{extpyr}	Mass Mean Radius Extraneous Pyrite (cm)
R_f	Rate of CO Oxidation (mole s^{-1})
r_{glass}	Radius of Glass Particle (cm)
r_{pyr}	Mass Mean Radius Inherent Pyrite (cm)
r_{sil}	Mass Mean Radius Inherent Silicate (cm)
SA_{char}	External Surface Area Char (cm^2)
SA_{extpyr}	External Surface Area Extraneous Pyrite (cm^2)
SA_{pyr}	External Surface Area Pyrite (cm^2)
SA_{sil}	Surface Area Silicates (cm^2)
(Sil)	Mass of Silicates on Char Surface (g)
T_g	Gas Temperature (K)
T_p	Char Temperature (K)
T_{pyr}	Extraneous Pyrite Temperature (K)
V_g	Gas Volume (cm^3)
X_g	Probability of Iron-Silicate Contact
y	Fitted Mass Silicates Consumed for Glass Formation (g)
ΔH_c	Heat of Combustion for Char (cal g^{-1})
ΔH_r	Heat of Reaction for Pyrrhotite (cal g^{-1})
γ	Surface Tension Silicate Melt (dyne cm^{-1})
ϵ	Emissivity
σ	Stefan-Boltzmann Constant ($\text{cal sec}^{-1} \text{cm}^{-2} \text{K}^{-4}$)
ρ_{glass}	Density of Glass (g cm^{-3})

Model Variable Definitions (cont'd)

Variable	Definition
ρ_{sil}	Density of Silicates (g cm^{-3})
ρ_{pyr}	Density of Pyrite (g cm^{-3})
μ	Viscosity of Silicate Melt ($\text{g cm}^{-1} \text{s}^{-1}$)

Chapter 6

6. Conclusions and Future Work

As iron has long been known to play a major role in slagging and fouling in coal fired boilers, this work set out to elucidate the mechanisms for iron-silicate interactions during combustion. It was hoped that these mechanisms, and the pyrite oxidation mechanisms in the literature, could be used to develop a comprehensive model to predict iron partitioning during the combustion of pulverized coal.

In order collect data on the iron-silicate interactions, a suite of well characterized coals were burned, under a wide range of experimental conditions, in a 17kWh downfired laboratory scale combustor. Fly ash samples were then collected and analyzed by a number of diverse techniques. These techniques included Atomic Absorption (AA), Scanning Electron Microscopy coupled with Energy Dispersive X-Ray (SEM-EDX), Transmission Electron Microscopy (TEM), and X-Ray Diffraction (XRD). Mössbauer and Computer Controlled Scanning Electron Microscopy (CCSEM) were particularly important.

Three different pathways were proposed for iron-silicate interactions: gas phase coagulation of pyrite and silicate particles, iron fume interaction with extraneous silicates, and inherent mineral interactions. From the experimental conditions and AA derived data two of the proposed mechanisms, coagulation and iron fume

formation, could be neglected. Therefore the dominant pathway for iron-silicate interactions involved only the inherent mineral matter. Two mechanisms were proposed for the inherent mineral matter interactions. In one proposed mechanism iron and silicates exist in the combustion zone as a melt from which iron oxide crystallizes as the melt cooled. Agglomeration of iron and silicate particles during char burnout was proposed as the second possible mechanism.

In order to differentiate between the two mechanisms a number of the previously mentioned analytical tools were brought to bear on selected ash samples. These techniques found no iron oxide particles in a silicate melt (TEM) and direct evidence of iron oxide and silicate particles in ash particle agglomerates (SEM-EDX). Therefore, the agglomeration mechanism was found to be the primary pathway for iron-silicate interactions.

The agglomeration mechanism was then used, in conjunction with many mechanisms and models from the literature, to derive a comprehensive model to predict iron partitioning during the combustion process. The important mechanisms (and kinetic parameters) derived from the literature included pyrite oxidation, char burnout, and particle energy balances. The mechanisms and kinetics for iron capture by silicates (glass formation) during char burnout represents the major contribution of this work. The mechanism was derived from particle-particle sintering work in the literature and a probability (proposed by the author) of two particles coming in contact to form the

glass. The kinetics for glass formation was assumed to have an Arrhenius form and contained one of the two fit parameters in this model. This fit parameter, the preexponential rate constant, was found (by a least squares fit of the data) to be $10^{112.5}$ (g glass sec^{-1} cm^2 silicate $^{-1}$). The temperature dependence was that for iron diffusing through silicate melts from the literature (Turkdogan, 1985). The second fit parameter, the amount of silicates consumed per amount iron consumed, was found (by multivariable least squares fit) to be 8.1.

The model predicted fraction of iron in the glass and pyrrhotite phases correlated well with the measured fraction of iron in those phases. The model was then used (in conjunction with the experimental data) to explore the effects of several variables on iron partitioning. The first variable, peak char temperature, had little or no effect on the iron in the glass and pyrrhotite phase. This suggests that pyrrhotite, rather than molten iron oxide, is the dominant iron form captured by the silicates. The next variable tested, the ratio of inherent silicate to total iron in the coal, had a pronounced effect on the iron partitioning. Within the range of this variable tested (approximately 1.5 to 19.4) the amount of iron in the glassy phase increased as this ratio increased. This suggests that as the amount of inherent silicate in the coal increases, the opportunity for the pyrite to oxidize and solidify decreases. If, on the other hand, this ratio decreases, the silicates can capture less of the iron and the pyrite has a greater opportunity to oxidize. The final variable tested, the stoichiometric ratio, also had a large effect on the iron partitioning. In this case the

fraction of iron in the glass and pyrrhotite phases increased dramatically with decreasing (primarily substoichiometric) stoichiometric ratios. This was caused by residual unoxidized pyrrhotite as the fraction as glass was found to remain essentially constant.

Although this work was successful in developing a model to predict iron partitioning during combustion, future work in this area should further test the model assumptions and parameters and use the model (and others) to develop a more robust model to predict slagging and fouling in power boilers. For example, one major assumption in the pyrite oxidation kinetics was the use of a fit to calculate the liquid mass transfer coefficient as a function of the gas mass transfer coefficient. One way to get a better understanding of this parameter would be to perform some bench scale studies with pure pyrite of known size. Then, by assuming the other kinetic parameters in the literature are valid, it may be possible to determine the effect of temperature and particle size on the liquid mass transfer coefficient.

Another important parameter that may be clarified with further work in bench scale studies is the fit parameter y (mass silicates consumed per g iron captured in the glass). For example, if the fit parameter is a function of the particle time temperature history and quench rate (crystallization rates or melt dissolution rate), the fitted parameter would be very different for bench scale data. If, however, the parameter is an average parameter based on some other mechanism, the model

should be able to correctly predict the fraction iron as glass for the bench scale as well as the larger scale.

Although some substoichiometric experiments were successful utilizing the laboratory scale combustor, it would also be useful to use bench scale experiments to explore the effect of stoichiometric ratio on both the coal derived pyrites and pure pyrites. By using a smaller scale, with fewer potential oxygen leaks, better control of the stoichiometric ratio may be achieved. This data could then be used to either substantiate the findings from this work or clarify mechanisms that may be hidden in the larger scale combustor.

Other areas of interest for future work include the use of a burnable beneficiated coal to test the current model and highlight any weaknesses. Coals of different ash compositions and coal types would also be of interest. For example, the sub-bituminous coal in this study contained a large amount of finely divided calcium and a very low iron content. Another sub-bituminous coal with either lower calcium or (more likely) calcium in the form of large calcite inclusions, would widen the composition-coal type matrix used in this study. Similarly, coals with extraneous pyrite fractions lower than 25% or greater than 50% could be used to further test the effect of the inherent silicate to total iron ratio (Chapter 5) on iron partitioning.

Although most of the future work proposed thus far has involved refining the current

model, another very important area is the use of the model to develop strategies to predict slagging and fouling in boilers. The current model is strictly limited to the partitioning of iron in the ash. However, in order to predict the true slagging or fouling propensities of a given coal other information should be taken into account. For example, other mineral species (alkalis and finely divided calcium, for example) have also been implicated in slagging and fouling problems. Therefore, a model should be developed that takes into account the behavior of the other problematic species as well as the iron. Further, the amount of ash in the coal per btu may be important in the growth rate of deposits. For example, the Eagle Butte in this study has been found to produce very sticky ash. However, there is very little ash in the coal. Would this, therefore, cause fewer problems than another coal that produces slightly sticky ash in higher quantities? In order to create and test this type of model, a good method needs to be derived to quantify the ash loss (by slagging) in the furnace. If, for example, the difference in measured ash concentration and predicted ash concentration (Chapter 4, Appendix C) is a good measure of how much material (slag) is lost to the wall, it may be possible to develop a comprehensive strategy to predict slagging and fouling in a boiler.

Appendix A: Fraction Oxide Plots

As mentioned in Section 4.2, AA played a minor role in this work. Most of the AA data obtained as part of this work has either already been presented (Sections 4.2 and 4.5) or is presented by Gallagher (1992). The following figures represent the miscellaneous AA data collected as part of this work and not yet presented (AA samples were not collected or, if collected, analyzed for all experiments).

Figure A.1 Fraction Oxide Plot for Run 56 Low; Kentucky No. 11

Figure A.2 Fraction Oxide Plot for Run 56 High; Kentucky No. 11

Figure A.3 Fraction Oxide Plot for Run 57; Kentucky No. 11

Figure A.4 Fraction Oxide Plot for Run 58; Kentucky No. 11

Figure A.5 Fraction Oxide Plot for Run 64; Eagle Butte

Figure A.5 Fraction Oxide Plot for Run 67; Kentucky No. 9

Appendix B: Mössbauer Spectra

The following figures show the Mössbauer spectra available to the author at the time this dissertation was written. In many cases only the quantitative iron distributions (Table 4.4.1) were sent to the University of Arizona from the University of Kentucky. Figures B.1 through B.4 represent the only University of Kentucky derived spectra available. However, for those samples analyzed at the University of Arizona (Table 4.4.2) the individual spectrum were also available.

The raw Mössbauer spectra consist of a number of counts in each individual channel (channels number 1 through 512). The channels can then be converted to particle velocities according to equation B.1. The constants A and B are determined from calibrations with metallic iron ($A=0.03852$, $B=9.83511$ were used here). The transmittance was calculated by defining the count rate in the first channel as 100% transmittance. For the first two University of Arizona derived spectra (Figures B.5 and B.6) the gamma source was still fairly strong, therefore the signal to noise ratio was fairly high. For all of the subsequent samples, however, the source had decayed considerably. In order to better determine the peak locations, these spectra (Figures B.7 through B.20) were smoothed over 10 points. The actual quantitative analysis used the raw, unsmoothed data.

Figure B.1 Mössbauer Spectrum from Run 56A; Kentucky No. 11 (University of Kentucky)

Figure B.2 Mössbauer Spectrum from Run 56D; Kentucky No. 11 (University of Kentucky)

Figure B.3 Mössbauer Spectrum from Run 57A; Kentucky No. 11 (University of Kentucky)

Figure B.4 Mössbauer Spectrum from Run 58C; Kentucky No. 11 (University of Kentucky)

Figure B.5 Mössbauer Spectrum from Run 56C; Kentucky No. 11 (University of Arizona)

Figure B.6 Mössbauer Spectrum from Run 56F; Kentucky No. 11 (University of Arizona)

Figure B.7 Mössbauer Spectrum from Run 61B; Eagle Butte (University of Arizona)

Figure B.8 Mössbauer Spectrum from Run 64A; Eagle Butte (University of Arizona)

Figure B.9 Mössbauer Spectrum from Run 67C; Kentucky No. 9 (University of Arizona)

Figure B.10 Mössbauer Spectrum from Run 68; Kentucky No. 9 (University of Arizona)

Figure B.11 Mössbauer Spectrum from Run 69A; Kentucky No. 9 (University of Arizona)

Figure B.12 Mössbauer Spectrum from Run 69B; Kentucky No. 9 (University of Arizona)

Figure B.13 Mössbauer Spectrum from Run 70B; Illinois No. 6 (University of Arizona)

Figure B.14 Mössbauer Spectrum from Run 70C; Illinois No. 6 (University of Arizona)

Figure B.15 Mössbauer Spectrum from Run 71; Upper Freeport (University of Arizona)

Figure B.16 Mössbauer Spectrum from Run 72; Kentucky No. 11 (University of Arizona)

Figure B.17 Mössbauer Spectrum from Run 73B; Kentucky No. 11 (University of Arizona)

Figure B.18 Mössbauer Spectrum from Run 73E; Kentucky No. 11 (University of Arizona)

Figure B.19 Mössbauer Spectrum from Run 74C; Kentucky No. 11 (University of Arizona)

Figure B.20 Mössbauer Spectrum from Run 74E; Kentucky No. 11 (University of Arizona)

Appendix C: Ash Mass Concentrations

The following table, Table C.1, shows the average ash mass concentration in the furnace for several experiments. This information could be used to convert the mass fraction plots in Section 4.5 to ash mass concentration distributions. As can be seen from the table, this total ash mass concentration was calculated by two different methods. The first method, denoted as 'AA' in the table, utilized the total mass collected in the impactor and the total flue gas sampled. The second method, denoted as 'Foster Wheeler', used the total ash feedrate (from the percent ash in the coal and the coal feedrate) and the flue gas rate. These results from these methods were often very different. The percent difference shown in the table was calculated as the difference between the techniques divided by the result of the Foster Wheeler analysis. The reasons for this discrepancy is not known, but may include sampling errors and ash losses to the wall.

Table C.1 Ash Mass Concentrations

Run	Coal	Ash Conc. (mg/m ³)		% Diff
		AA	Foster Wheeler	
13	BL	3369.067	16016.93	78.97
14	BL	2054.199	15498	86.75
15	EB	1594.495	6938.903	77.02
16	EB	2118.897	7337.462	71.12
17	K9	4243.826	14670.82	71.07
18	K9	4918.318	14977.62	67.16
19	I6	5240.207	10643.76	50.77
20	I6	6752.749	10027.13	32.66
27	K11	6655.433	24016.62	72.29
28	K11	10251.63	24246.33	57.72
32	UF	8998.929	27139.6	66.84
33	UF	12117.07	26569.55	54.39
34	UF	10583.07	27139.6	61.01
35	UF	5253.469	27139.6	80.64
36high	K9	6624.439	14363.98	53.88
36low	K9	9215.317	14106.06	34.67
37high	K11	10499.37	23317.13	54.97
37low	K11	9919.649	22948.21	56.77
38high	BL	1363.319	16049.19	91.51
38low	BL	1439.955	16419.83	91.23
40high	EB	222.209	6963.532	96.81
40low	EB	957.608	7038.981	86.40

Appendix D

D. Residence Time Calculations

One of the important input parameters for the iron partitioning model was the time-temperature history for each experiment. However, when the temperature profile was measured as part of the experimental procedure, it was a distance-temperature profile. In order to convert between this experimentally measured distance-temperature profile to a time-temperature profile needed as a model input, the residence time at each port was calculated. This resulted in time-temperature data for each condition which could then be curve fitted for use in the model as described in Chapter 5.

The first step in calculating the residence time at each port was to determine the flue gas rate (Q , slpm) in the furnace, based on the the input air rates and the stoichiometric ratio for the experiment (assuming complete combustion). The measured distance-temperature profile was then curve fitted to Equation D.1. Assuming ideal gas behavior, constant pressure, and plug flow in the furnace, the flue gas velocity could then be calculated according to Equation D.2. The furnace crosssectional area (CSA_{furn}) was allowed to vary as shown in Figure D.1. The residence time (τ) was calculated according to Equation D.3 using a four point Simpson's technique for the integrations. The residence times calculated by this method were very similar to those calculated by Gallagher who used a slightly different technique.

$$T = A_1 \exp(A_2(A_3+z)) (1-\exp(A_4(A_3+z))) \quad (D.1)$$

$$v = \frac{Q}{CSA_{furn}} \frac{T}{298} \quad (D.2)$$

$$\tau = \left(\frac{\int_{x=0}^{x=z} v \, dx}{\int_{x=0}^{x=z} dx} \right)^{-1} z \quad (D.3)$$

Figure D.1 Schematic of Upper Section of Furnace

Appendix E: Fortran Codes

E.1: Input Paramteer Listings

The following variables are the experimental parameters and model parameters needed as input parameters:

```

CON(1):  Gas temperature fit parameter,  $A_2$ , discussed in Chapter 5
CON(2):  Gas temperature fit parameter,  $A_1$ , discussed in Chapter 5
CON(3):  Gas temperature fit parameter,  $A_4$ , discussed in Chapter 5
CON(4):  Gas temperature fit parameter,  $A_3$ , discussed in Chapter 5
CON(10): Measured fraction iron as glass and pyrrhotite
CRUN:    A 6 character identification string for a specific experiment
DELTA0:  Parameter used in ODE solver to control step size
H0:      Initial step size
EG:      Temperature Dependence of glass formation ( $E_g$ ), discussed in
          Chapter 5
FEOUT:   Fraction original pyrite remaining to assume reactions complete
GF:      Fit parameter ( $y$ ), discussed in Chapter 5
GK:      Fit parameter ( $G_k$ ), discussed in Chapter 5
HNEW:    An imposed maximum step size
IDCOAL:  Numerical identifier for the coal (used to identify coal in
          CDAT.FOR)
IFILE:   Parameter to control how much data is printed to files (1=all
          data, 2=only iron distribution and maximum temperatures)
IPRINT:  The number of steps to be taken before output is recorded
ISCREEN: Parameter to control what data is displayed on screen (1=gas
          mole fractions, 2=temperatures, 3=fraction conversion for
          extraneous pyrite, 4=iron distribution)
MAXIT:   Maximum iterations allowed
NPRINT:  Controls whether intermediate data is displayd on screen or only
          final fraction iron as glass and pyrrhotite (1=intermediate,
          2=only final)
NPTS:    The number of experiments to be simulated
SR:      Stoichiometric ratio
TOUT:    Residence time for Port 11, assumes if combustion/reaction is
          not complete by this time it is frozen
TOFFSET: Gas temperature fit parameter,  $A_5$ , discussed in Chapter 5

```

Format for Input File (PART.DAT)

```

NPTS,MAXIT,NPRINT,HNEW
H0,DELTA0,FEOUT,IPRINT,ISCREEN,IFILE
TCRYST,TMELT,GK,GF,EG
CRUN
CON(1),CON(2),CON(3),CON(4),CON(10),SR,IDCOAL,TOUT
TOFFSET

```

Input File Used for This Work (PART.DAT)

```

26,1000000,1,1.E-2
1.E-6,0.001,1E-2,500,4,1
1600,1353,10112.5,8.1,12573
RUN67
0.200,1750,6.00,0.0400,0.23,1.30,4,3.43,0
0.0
RUN68
0.250,1750,6.00,0.0300,0.23,1.20,4,3.31,0
0.0
RUN69A
0.53,2250,5.,0.0760,0.363,1.18,4,2.25,0
0.0
RUN21
0.152,1775,7.79,0.0235,0.16,1.27,7,3.49,0
0.0
RUN47B
0.090,1700,7.50,0.0500,0.18,1.30,7,3.49,0
0.0
RUN47H
0.150,1800,7.20,0.0240,0.32,1.32,7,2.88,0
0.0
RUN70B
0.280,1910,12.0,0.0410,0.256,1.20,7,1.86,0
0.0
RUN27
0.127,1780,5.30,0.0350,0.26,1.25,6,3.83,0
0.0
RUN56C
0.070,1610,6.60,0.0400,0.23,1.25,6,5.07,0
0.0
RUN56F
0.141,1780,10.8,0.0170,0.33,1.20,6,2.83,0
0.0
RUN57
0.040,1450,5.00,0.0600,0.45,0.8,6,4.18,1
0.0
0.25
RUN58
0.150,1835,10.0,0.020,0.39,1.32,6,3.911,2
0.0
0.7569,0.216
R72
1.000,1800,123.,0.7000,0.763,0.715,6,4.052,0
1000
R73B
0.700,1275,3.20,0.0001,0.660,0.79,6,4.346,0
800
R73E
0.160,1750,7.00,0.0001,0.340,1.000,6,3.842,0
0
R74C
0.70,1000,3.20,0.0001,0.690,0.790,6,7.554,0
800
R74E
0.650,1300,1.70,0.0001,0.458,0.900,6,6.313,0
800

```

This program was designed to solve the set of ODE's defined in Chapter 5. The program consists of a main program, an ODE solver package, subroutines to define the differential equations and the jacobian, and subroutines to calculate the various parameters utilized in the differential equations.

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCC      THIS IS THE MAIN PROGRAM THAT CALLS TYSONLPK  CCCCCCCCCCCCC
CCCCC      AND CONTROLS PRINTOUT TIMES                    CCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      PROGRAM IRONPART
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*8 COAL,COALNAM
      CHARACTER*12 INFNAM,OFNAM
      CHARACTER*6 CRUN
      EXTERNAL FUN,JAC,DFDX
      DIMENSION Y(50),YDOT(50),ERRPHI(50),CON(25),DAT(25),COAL(6)
      DIMENSION SIZET(10),SIZER(10)
      INCLUDE 'MODCON.COM'

```

CCCCCCC OPEN APPROPRIATE INPUT AND OUTPUT FILES CCCCCCCCCCCCCCCC

```
OPEN(4,FILE='PART.DAT',STATUS='OLD')
OPEN(3,FILE='RESULT.OUT',STATUS='UNKNOWN')
OPEN(16,FILE='TMAX.OUT',STATUS='UNKNOWN')
OPEN(23,FILE='GLASS.OUT',STATUS='UNKNOWN')
```

CCCCCCC READ INPUT VALUES FROM PART.DAT CCCCCCCCCCCCCCCCCCCCCC

```
READ(4,*)NPTS,MAXIT,NPRINT,HNEW
READ(4,*)H0,DELTA0,FEOUT,IPRINT,ISCREEN,IFILE
READ(4,*)TCRYST,TMELT,GK,GF,EG
```

```
WRITE(3,118)GK
WRITE(3,120)GF
WRITE(3,122)EG
WRITE(3,*)' '
WRITE(3,109)
```

```
IF(IFILE.EQ.2)GOTO 3
IF(NPRINT .EQ. 2)GOTO 3
OPEN(10,FILE='TMPS.OUT',STATUS='UNKNOWN')
OPEN(11,FILE='PHIS.OUT',STATUS='UNKNOWN')
OPEN(12,FILE='GASES.OUT',STATUS='UNKNOWN')
OPEN(15,FILE='PART.OUT',STATUS='UNKNOWN')
```

3

CONTINUE

```
IF(NPRINT .EQ. 2)WRITE(*,109)
SUM=0.0
```

CCCCCCC READ COAL SPECIFIC INFORMATION AND START "BURN" CCCCCCCC

DO 35 K=1,NPTS

```
READ(4, '(A)')CRUN
READ(4,*)CON(1),CON(2),CON(3),CON(4),CON(10),SR,IDCOAL,TOUT,IO2
READ(4,*)TOFFSET
```

CALL COALDAT(IDCOAL,DAT,COALNAM)

CCCCCCC SET COAL DATA (SEE COALDAT FOR DEFINITIONS) CCCCCCCCCCCCCCCCCC

```
DO 5 I=1,5
CON(I+4)=DAT(I)
```

5

CONTINUE

```
CON(11)=DAT(6)
CON(12)=DAT(7)
CON(13)=DAT(8)
CON(14)=DAT(9)
CON(15)=DAT(10)
CON(16)=DAT(11)
CON(17)=DAT(12)
CON(18)=DAT(13)
CRAD =DAT(14)
CRITT =DAT(15)
CON(19)=DAT(16)
CON(20)=DAT(17)
CON(21)=DAT(19)
CON(22)=DAT(20)
CON(23)=DAT(18)
```

```

CON(24)=DAT(21)
CON(25)=DAT(22)
XSIL   =DAT(23)

CCCCCCC      RESET INITIAL CONDITIONS AT START OF EACH COAL CCCCCC

      IF(NPRINT.EQ.1)WRITE(*,*) '      '

      H=HO
      DELTA=DELTAO
      T=0.0E0
      ITIME=0
      CHARO=4*3.14159*(CRAD**3)*1.5E6/3      !DEVOLATILIZED CHAR
      TOTCOAL=CHARO/(CON(19)+CON(23))      !TOTAL MASS COAL IN

      WATER=CON(21)*TOTCOAL/18      !MOISTURE IN (MOLES)

      CALL TEMP(T,CTEMP)

      Y(1)=CHARO      !MASS CHAR
      Y(2)=0.0E0      !MASS IRON GLASS
      Y(3)=0.0E0      !MASS INH. OXIDE
      Y(4)=0.0      !MASS EXTR. OXIDE
      Y(5)=298.0      !CHAR TEMP (K)
      Y(6)=GMOLO2-(CON(20)*TOTCOAL/24)      !TOTAL MOLES O2
      Y(7)=CON(20)*TOTCOAL/12      !MOLE CO IN BULK
      Y(8)=0.0      !MOLE CO2 IN BULK
      Y(9)=298.0      !EXTR. PYRITE TEMP (K)
      Y(10)=0.0

      SIO2=0.0E0
      PYRO=0.0E0
      IMELT=0
      PYRATIO=1.0
      IMELT2=0
      IMELTSI=0
      PTMAX=298
      STMAX=298
      CTMAX=298
      IOXIDE=0
      IO=0
      FES=0.0

CCCCCCC      CALCULATE CONSTANTS FOR USE LATER CCCCCCCCCCCCCCCCCCCCCC

      DENSCORR=5.E6*3.14159*4/3
      ASHMASS=TOTCOAL*(CON(6)+CON(7))

CCCCCCC      WRITE INTIAL CONDITIONS INTO OUTPUT FILES CCCCCCCCCCCCCCCCCC

      XC=1
      WPi=CON(7)/(CON(7)+CON(9))
      WPe=CON(9)/(CON(7)+CON(9))
      WOi=0.0
      Woe=0.0
      WG=0.0
      IF (NPRINT .EQ. 2)GOTO 7
      IF(ISCREEN.EQ.4)WRITE(*,98)
      IF(ISCREEN.EQ.4)WRITE(*,99)T,XC,WG,Woi,Woe,Wpi,Wpe
7      CONTINUE

```

```

CCCCC      TYSONLPK PARAMETERS ARE SET HERE      CCCCCCCCCCCCCCCCCC

      NEQ=10
      NBUG1=0
      NBUG2=0
      IN=0

CCCCC CALL TYSONLPK UNTIL THE OUTPUT VALUE OF FESX IS REACHE CCCCCC
CCCCC      PRINTING RESULTS AT EACH GIVEN TIME INTERVAL      CCCCCC

      DO 40 IOUT = 1,MAXIT
      CALL TYSON(FUN,JAC,DFDX,NEQ,Y,T,H,NBUG1,NBUG2,DELTA,IN)

CCCCC DETERMINE PO2 AND TEMPERATURE AT EACH STEP CCCCCCCCCCCCCCCCCC

      TOP=1.-(Y(1)/CHAR0)
      BOT=1.-(ASHMASS/CHAR0)
      CX=(TOP/BOT)

      STEMP=Y(5)
      PTEMP=Y(9)
      CALL TEMP(T,CTEMP)

      IF(STEMP.GT.STMAX)STMAX=STEMP
      IF(PTEMP.GT.PTMAX)PTMAX=PTEMP
      IF(CTEMP.GT.CTMAX)CTMAX=CTEMP

      WATER=(CON(21)*TOTCOAL/18)+(CX*TOTCOAL*CON(22)/36)
      TOTMOL=Y(6)+WATER+Y(7)+Y(8)+GMOLN2
      V=TOTMOL*82.06*CTEMP

      YO2=Y(6)/TOTMOL
      YCO=(Y(7))/TOTMOL
      YCO2=(Y(8))/TOTMOL
      YN2=GMOLN2/TOTMOL
      YH2O=WATER/TOTMOL

CCCCC DETERMINE PHI AT EACH TIME STEP CCCCCCCCCCCCCCCCCC

      PRAD=CON(11)/2.0
      PRADCM=PRAD*100

      PMASS=4*3.14159*(PRADCM**3)*5.0/3
      PYROHIT=PMASS-(Y(4)/0.827)
      PYRATIO=PYROHIT/PMASS
      IF(PYRATIO .LT. 0.0)PYRATIO=0.0

      TOTFE=TOTCOAL*(CON(9)+CON(7))

      W4=0
      W5=0
      W6=0
      W7=0
      W8=0.0
      W1=(Y(2))/(GF+1)
      W2=Y(3)/(0.827)
      W9=Y(10)/(0.827)
      W3=(1-PYRATIO)*CON(9)*TOTCOAL
      W10=0.0
      W11=0.0
      IF(STEMP.GT.TMELT)W4=(TOTCOAL*CON(7)-W1-W2-W9)
      IMF GLASS
      IMF SOLID OXIDE
      IMF INH. LIQUID OXIDE
      IMF EXTRAN. OXIDE

```



```

IF (PTEMP.GT.TMELT) W5=(PYRATIO*CON(9)*TOTCOAL)
IF (STEMP.LE.1353) W6=(TOTCOAL*CON(7)-W1-W2-W9)
IF (PTEMP.LE.1353) W7=(PYRATIO*CON(9)*TOTCOAL)
IF (STEMP.GT.TCRYST) W10=W9
IF (STEMP.GT.1415) W11=W1
IF (W4.LT.0) W4=0.0
IF (W6.LT.0) W6=0.0
WPYR=W4+W6
WEXT=W5+W7
PHIC=0.0
PHIG=0.0
PHIMOS=0.0

```

```
CALL PYRITE(Y,STEMP,PYRO)
```

```

BOTT=W1+W2+W3+W4+W5+W6+W7+W9+W8      !TOTAL Fe AS PYR. (G)
BOTTINH=BOTT-WEXT-W3-W8                !TOTAL INH. Fe AS PYR. (G)
IF (BOTT.LE.0) GOTO 9

```

```

PHIG=W1/BOTT                          !MF GLASS
PHIMOS=(W1+W4+W6+W5+W7)/BOTT          !MF GLASS & PYRH.

```

```

PHIG=(1-Xsil)*PHIG+Xsil                !MF GLASS
PHIMOS=(1-Xsil)*PHIMOS+Xsil            !MF GLASS & PYRH.

```

```
9      CONTINUE
```

```
CCCCC DETERMINE PYRITE AND SILICATE MASS AT EACH STEP CCCCCCCCCCCCCCCC
```

```
IF ((IMELTSI.EQ.0).AND.(STEMP.GT.CRITT)) IMELTSI=1
```

```

CALL SIL(Y,STEMP,SIO2)
CALL PYRITE(Y,STEMP,PYRO)

```

```

IF (PYRO .LT. 0.0) WRITE(*,*) 'ABORT RUN, PYRO.lt.0'
IF (PYRO .LT. 0.0) GOTO 60

```

```

IF ((H .GT. HNEW).and.(STEMP.LT.900)) H=HNEW
IF ((H .GT. HNEW).AND.(STEMP.LT.900)) DELTA=DELTAO

```

```

IF (H.LT.HO) H=HO
IF (DELTA.LT.DELTAO) DELTA=DELTAO

```

```
CCCCC DETERMINE MASS FRACTIONS OF SPECIES ON SURFACE CCCCCCCCCCCCCCCC
```

```

IF (STEMP.GE.TMELT) IMELT=1
IF (PTEMP.GT.TMELT) IMELT2=1
IF ((STEMP.GT.TCRYST).AND.(IOXIDE.EQ.0)) IOXIDE=1

```

```

WG=W1/BOTT
WOi=(W2+W9)/BOTT
WOe=(W3+W8)/BOTT
WPI=WPYR/BOTT
WPe=WEXT/BOTT
XC=1-(TOP/BOT)
IF (WPI.LT.0.0) WPI=0.0
IF (XC.LT.0.0) XC=0.0
WL=(Y(10))/BOTT
ERR=ABS(CON(10)-PHIMOS)
ESQ=ERR**2

```

CCCCC PRINT DATA AFTER THE IPRINT NUMBER OF STEPS CCCCCCCCCCCCCCCCCC

```

IF(NPRINT .EQ. 2)GOTO 13
IF(IFLAG. NE. IPRINT)GOTO 13
  IF(ISCREEN.EQ.1)WRITE(*,113)XC,YO2,YCO,YCO2,YH2O,YN2
  IF(ISCREEN.EQ.2)WRITE(*,114)T,XC,CTEMP,STEMP,PTEMP,PYRATIO
  IF(ISCREEN.EQ.3)WRITE(*,115)T,XC,PHIMOS
  IF(ISCREEN.EQ.4)WRITE(*,99)T,XC,WG,Woi,Woe,Wpi,Wpe
  IF(ISCREEN.EQ.5)WRITE(*,107)T,CTEMP,STEMP,WPI,WL,Woi

  IF(IFILE.EQ.1)WRITE(15,99)T,XC,WG,Woi,Woe,Wpi,Wpe
  IF(IFILE.EQ.1)WRITE(12,113)XC,YO2,YCO,YCO2,YH2O,YN2
  IF(IFILE.EQ.1)WRITE(10,114)T,XC,CTEMP,STEMP,PTEMP,PYRATIO
  IF(IFILE.EQ.1)WRITE(11,115)T,PEXTR,PINH
  IFLAG=0
13  CONTINUE
  IFLAG=IFLAG+1

```

CCCCC BOUNCE OUT OF LOOP IF OUTPUT CRITERION ARE REACHED CCCCCCCCCCCCCC

```

IF(Y(1).GT.ASHMASS)GOTO 15
IF(PYRATIO .GT. 0.001)GOTO 15
  IF(Wpi.GT.FEOUT)GOTO 15
    IF(NPRINT .EQ. 2)GOTO 14
      IF(ISCREEN.EQ.1)WRITE(*,113)XC,YO2,YCO,YCO2,YH2O,YN2
      IF(ISCREEN.EQ.2)WRITE(*,114)T,XC,CTEMP,STEMP,PTEMP,PYRATIO
      IF(ISCREEN.EQ.3)WRITE(*,115)T,XC,PHIMOS
      IF(ISCREEN.EQ.4)WRITE(*,99)T,XC,WG,Woi,Woe,Wpi,Wpe

      IF(IFILE.EQ.1)WRITE(15,99)T,XC,WG,Woi,Woe,Wpi,Wpe
      IF(IFILE.EQ.1)WRITE(12,113)XC,YO2,YCO,YCO2,YH2O,YN2
      IF(IFILE.EQ.1)WRITE(10,114)T,XC,CTEMP,STEMP,PTEMP,PYRATIO
      IF(IFILE.EQ.1)WRITE(11,115)T,PEXTR,PINH
14  CONTINUE

  WRITE(*,111)PHIMOS,CON(10),CRUN,COALNAM
  WRITE(23,111)PHIG,CON(10),CRUN,COALNAM
  WRITE(3,111)PHIMOS,CON(10),CRUN,COALNAM
  WRITE(16,116)CTMAX,STMAX,PTMAX,CRUN,COALNAM

  ERRPHI(K)=ABS(PHIMOS-CON(10))
  SUM=SUM+(ERRPHI(K)**2)
  RELERR=ERRPHI(K)/CON(10)

```

```

      GOTO 30
15  CONTINUE

  IF(STMAX.LT.1000)GOTO 17
  IF(STEMP.GE.1000)GOTO 17
  IF(NPRINT.EQ.2)GOTO 16
    IF(ISCREEN.EQ.1)WRITE(*,113)XC,YO2,YCO,YCO2,YH2O,YN2
    IF(ISCREEN.EQ.2)WRITE(*,114)T,XC,CTEMP,STEMP,PTEMP,PYRATIO
    IF(ISCREEN.EQ.3)WRITE(*,115)T,XC,PHIMOS
    IF(ISCREEN.EQ.4)WRITE(*,99)T,XC,WG,Woi,Woe,Wpi,Wpe
    IF(IFILE.EQ.1)WRITE(15,99)T,XC,WG,Woi,Woe,Wpi,Wpe
    IF(IFILE.EQ.1)WRITE(12,113)XC,YO2,YCO,YCO2,YH2O,YN2
    IF(IFILE.EQ.1)WRITE(10,114)T,XC,CTEMP,STEMP,PTEMP,PYRATIO
    IF(IFILE.EQ.1)WRITE(11,115)T,PEXTR,PINH
16  CONTINUE

```

```

WRITE(*,111)PHIMOS,CON(10),CRUN,COALNAM
WRITE(23,111)PHIG,CON(10),CRUN,COALNAM
WRITE(3,111)PHIMOS,CON(10),CRUN,COALNAM
WRITE(16,116)CTMAX,STMAX,PTMAX,CRUN,COALNAM

ERRPHI(K)=ABS(PHIMOS-CON(10))
SUM=SUM+(ERRPHI(K)**2)
RELEERR=ERRPHI(K)/CON(10)

GOTO 30

17      CONTINUE

IF (T .LE. TOUT)GOTO 19
IF(NPRINT .EQ. 2)GOTO 18
      IF(ISCREEN.EQ.1)WRITE(*,113)XC,YO2,YCO,YCO2,YH2O,YN2
      IF(ISCREEN.EQ.2)WRITE(*,114)T,XC,CTEMP,STEMP,PTEMP,PYRATIO
      IF(ISCREEN.EQ.3)WRITE(*,115)T,XC,PHIMOS
      IF(ISCREEN.EQ.4)WRITE(*,99)T,XC,WG,Woi,Woe,Wpi,WPe
      IF(IFILE.EQ.1)WRITE(15,99)T,XC,WG,Woi,Woe,Wpi,WPe
      IF(IFILE.EQ.1)WRITE(12,113)XC,YO2,YCO,YCO2,YH2O,YN2
      IF(IFILE.EQ.1)WRITE(10,114)T,XC,CTEMP,STEMP,PTEMP,PYRATIO
      IF(IFILE.EQ.1)WRITE(11,115)T,PEXTR,PINH
18      CONTINUE
      WRITE(*,111)PHIMOS,CON(10),CRUN,COALNAM
      WRITE(23,111)PHIG,CON(10),CRUN,COALNAM
      WRITE(3,111)PHIMOS,CON(10),CRUN,COALNAM
      WRITE(16,116)CTMAX,STMAX,PTMAX,CRUN,COALNAM

      ERRPHI(K)=ABS(PHIMOS-CON(10))
      SUM=SUM+(ERRPHI(K)**2)
      RELEERR=ERRPHI(K)/CON(10)

19      CONTINUE

CCCCCCCCCCCCCCCC      FORMAT STATEMENTS      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

98      FORMAT(1X,' TIME',2X,'XCHAR',2X,'XGLS',2X,' XOXi',2X,' XOXe',2X,
1      'XPYi',2X,'XPYe')
99      FORMAT(1X,F5.3,2X,F5.3,2X,F5.3,2X,F5.3,2X,F5.3,2X,F5.3,2X,F5.3)
101     1      FORMAT(2X,'TIME(S)',4X,'SIL(MOL)',2X,'FESX(MOL)',4X,'CHAR(G)',
1      2X,'GLASS(MOL)',1X,'FE3O4(MOL)')
103     1      FORMAT(2X,'TIME(S)',4X,' PHI ',2X,'PYRATIO',4X,' Y4 ')
105     1      FORMAT(2X,'PHI=',1X,F5.3,1X,'FOR',1X,A8)
107     1      FORMAT(2X,f5.3,3X,F6.1,3X,F6.1,3X,F5.3,3X,F5.3,3X,F5.3)
109     1      FORMAT(2X,'MODEL',3X,'DATA',3X,'RUN ID',3X,'COAL NAME')
111     1      FORMAT(2X,F5.3,2X,F5.3,3X,A6,6X,A8)
113     1      FORMAT(3X,F5.3,3X,F5.3,3X,F5.3,3X,F5.3,3X,F5.3,3X,F5.3)
114     1      FORMAT(3X,F5.3,3X,F5.3,3X,F6.1,3X,F6.1,3X,F6.1,3X,F5.3)
115     1      FORMAT(3X,F5.3,3X,F5.3,3X,F5.3)
116     1      FORMAT(2X,F6.1,2X,F6.1,2X,F6.1,3X,A6,6X,A8)
118     1      FORMAT(2X,'GK=',1X,F7.1)
120     1      FORMAT(2X,'GF=',1X,F7.1)
122     1      FORMAT(2X,'EG=',1X,F7.1)
124     1      FORMAT(2X,'LEAST SQUARES:',1X,F5.3)
126     1      FORMAT(2X,' AVERAGE ERR :',1X,F5.3)
CCCCCCCCCC CALCULATE AND PRINT AVERAGE ABSOULUTE ERROR CCCCCCCCCCCCCCCCCC

40      CONTINUE
30      CONTINUE
35      CONTINUE

```



```

CCCCCCC DETERMINE CHAR OXIDATION CONST CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

R=1.987E-3

CHARK2=-CON(14)*EXP(-CON(13)/(STEMP*R))

CHARK1=-CON(14)*EXP(-CON(13)/(CTEMP*R))

CHARRAT=CHARK1/CHARK2

CCCCCCC GET DATA ON THE CHAR AND ASH CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

CALL DAT(PYRO,SIO2,Y,AREA,RAD,CMASS)      !GET ASH&CHAR INFO

CAREA=AREA(6)
CHRAD=RAD(1)

CCCCCCC CALCULATE THE EFFICIENCY CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

CALL EFF(CTEMP,PO2,CHARK2,CHRAD,SPO2,STEMP)

CCCCCCC CALCULATE CHAR BURNOUT RATE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

IF(Y(1).LE.ASHMASS)YDOT(1)=0.0
IF(Y(1).LE.ASHMASS)Y(1)=ASHMASS

IF(Y(1).GT.ASHMASS)YDOT(1)=CHARK2*AREA(6)*(SPO2**0.5)  !G C/SEC

IF(STEMP.LT. 600)YDOT(1)=0.0
IF(YDOT(1).EQ.0.0)SPO2=PO2

CCCCCCC DETERMINE ASH COMPONENT AREAS CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

FEL=0.0
FELI=0.0
IF(STEMP.LT.1353)PYRO2=0.0
IF(STEMP.GE.1353)PYRO2=PYRO
IF((IOXIDE.EQ.1).AND.(STEMP.GT.TCRYST))FEL=Y(10)

RHOG=(GF*2.5+5)/(1+GF)
DG3=(1/RHOG)*(1/(1+GF))*(2.5*(CON(17)**3)*GF+5.0*(CON(18)**3))
DG=DG3**0.3333333333

AG=6/(4*RHOG*DG)      !CSA GLASS/G
AP=6/(4*CON(18)*5.0)  !CSA PYR./G
AS=6/(4*CON(17)*2.5)  !CSA SIL./G

AS2=AS*4
AREAI=AP*(PYRO2+FEL)

AREAASH=(Y(3)+PYRO+Y(10))*AP+(Y(2))*AG+SIO2B*AS

IF(CAREA.LE.AREAASH)CAREA=AREAASH
IF(CAREA.LE.AREAASH)CHRAD=(AREAASH/(4*3.14159))**0.5

AFEL=FEL*AP
AFELI=FELI*AP
AASH=AREAASH
AL=AREAI

```

CCCCCCC DETERMINE GLASS FORMATION RATE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```
IF(CAREA.GT.AREAASH)X2=AREAI/(CAREA-AREAI)
IF(CAREA.LE.AREAASH)X2=AREAI/(AREAASH-AREAI)
IF(CAREA.GT.AREAASH)BOTa=(CAREA-AREAI)
IF(CAREA.LE.AREAASH)BOTa=(AREAASH-AREAI)
```

GCON=GK*AS2*SIO2*EXP(-EG/STEMP)

YDOT(2)=GCON*X2

CCCCCCCCC COMPUTE THE DIFFUSIVITY OF OXYGEN CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

TMEAN=(STEMP+CTEMP)/2

DIFF=2.4*((TMEAN/1800)**1.75)

AKoc=2*DIFF/con(18) !Gas Phase Mass Trans. (CM/SEC)

IF(STEMP.LE.1356)AKic=0.30*AKoc !From Srinavasachar

IF(STEMP.GT.1356)AKic=0.75*AKoc !From Srinavasachar

CCCCCCC DETERMINE IRON OXIDATION RATE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

C-----FOR LIQUID PYRRHOTITE -----C

```
IF(IMELT.NE.1)GOTO 5
AKtot=1/((1/AKoc)+(1/AKic))
AKD=61.78*AKtot*(SPO2)/(82.06*CTEMP)
YDOT(3)=AKD*PYRO*AREA(1)
IF(STEMP.GT.TCRYST)YDOT(3)=0.0
5 CONTINUE
```

C----- FOR SOLID PYRRHOTITE -----C

FEK=EXP(-18042/STEMP)*5E9 !From Srinivasachar (cm/sec)

AK=1/((1/AKoc)+(1/fek)+(1/(AKic))) ! (cm/sec)

IF(IMELT.NE.1)YDOT(3)=61.78*AK*AREA(1)*PYRO*SPO2/(82.06*CTEMP)

IF(STEMP.LT.900)YDOT(3)=0.0

CCCCCCC DETERMINE OXIDATION RATE OF EXTRANEIOUS MATERIAL CCCCCCCCCCCCCC

```
PRAD=CON(11)/2.0
PARE=4*3.14159*(PRAD**2)
PRADCM=PRAD*100
PARECM=4*3.14159*(PRADCM**2)
PTMEAN=(PTEMP+CTEMP)/2
RATIO=PTMEAN/101.68
```

PMASS=4*3.14159*(PRADCM**3)*5.0/3

PVOL=PMASS/5.0

PYROHIT=PMASS-(Y(4)/0.827)

IF(PYROHIT.LE.0.0)PYROHIT=0.0

IF(PYROHIT.EQ.0.0)GOTO 9

PRAT=PYROHIT/PMASS

IF(RATIO.LE.10.)SIG=-0.0175*RATIO+0.9174

```

IF(RATIO .GT. 10.)SIG=-0.0074*RATIO+0.8208

DIIFPy=2.4*((PTMEAN/1800)**1.75)
AKo=DIIFPy/(PRADCM)          !Gas Phase Mass Trans.

IF(PTEMP.GT.1356)AKi=0.75*AKo    !From Srinivasachar
IF(PTEMP.LE.1356)AKi=0.30*AKo    !From Srinivasachar

C----- FOR LIQUID PYRRHOTITE -----C

IF(IMELT2 .NE. 1)GOTO 7
  AKt=1/((1/AKo)+(1/AKi))
  AKDP=61.784*AKt/(82.06*PTMEAN)

  YDOT(4)=AKDP*PARECM*(PO2)
7  CONTINUE

C----- FOR SOLID PYRRHOTITE -----C

IF(IMELT2 .EQ. 1)GOTO 9
  FEKE=EXP(-18042/PTEMP)*5E9
  AKt=1/((1/FEKE)+(1/AKo)+(1/AKi))
  YDOT(4)=AKt*61.78*PARECM*PO2/(PTMEAN*82.06)
9  CONTINUE

IF(PTEMP .LT. 900)YDOT(4)=0.0
IF(PYROHIT .EQ. 0.0)YDOT(4)=0.0

CCCCCCC DETERMINE PARTICLE TEMPERATURE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

SIGMA=1.355E-12
EPS=0.8
CP=(4.03+0.00114*stemp-(204000./(STEMP**2)))/12.
TMEAN=(CTEMP+STEMP)/2

RATIO2=TMEAN/97.0
IF(RATIO2.LE.10)SIG2=-0.0205*RATIO2+1.0296
IF(RATIO2.GT.10)SIG2=-0.0081*RATIO2+0.9052
THERMK=5.7838e-5*((TMEAN/298)**0.75)
CK=THERMK/CHRAD

WALLT=0.98*CTEMP
DELHC=(25428.+0.82*STEMP+0.00033*STEMP**2+(213000./STEMP))/12.

CONVT=CK*(CTEMP-Y(5))
RADT=SIGMA*EPS*((WALLT**4)-(Y(5)**4))
TREAC=-YDOT(1)*DELHC

YDOT(5)=(CAREA*(CONVT+RADT)+TREAC)/(Y(1)*CP)

CCCCCCCC DETERMINE CONCENTRATIONS CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

CO2B=Y(6)/V          !BULK O2 CONC. (MOL/CC)
CCOB=Y(7)/V          !BULK CO CONC. (MOL/CC)
CCO2B=Y(8)/V         !BULK CO2 CONC. (MOL/CC)
CH2O=WATER/V         !BULK WATER CONC. (MOL/CC)

CCCCCCCC DETERMINE CO-CO2 TRANSFORMATION CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

RB=5.E8*V*EXP(-20130/CTEMP)*CCO2B
RF=3.9E14*V*EXP(-20130/CTEMP)*CCOB*(CH2O**0.5)*(CO2B**0.25)

```

```

      AKCO=DIFF*36*3.14159*CHRAD/1000.

      CCCCCCCCCC DETERMINE OXYGEN BALANCE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      YDOT(6)=(YDOT(1)/24.)+(0.5*(RB-RF))

      CCCCCCCCCC CO BALANCE IN BULK CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      YDOT(7)=(-YDOT(1)/12)+(RB-RF)

      CCCCCCCCCC CO2 FORMATION CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      YDOT(8)=(RF-RB)

      CCCCCC DETERMINE PYRITE TEMPERATURE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      SIGMA=1.355E-12
      EPS=0.5
      CPp=0.50
      PTMEAN=(CTEMP+PTEMP)/2
      THERMK=5.7838e-5*((PTMEAN/298)**0.75)
      CKP=THERMK/PRADCM
      WALLT=0.98*CTEMP
      IF(IMELT2.EQ.1)DELHP=4.544E4
      IF(IMELT2.NE.1)DELHP=4.810E4

      CONVTP=CKP*(CTEMP-Y(9))
      RADTP=SIGMA*EPS*((WALLT**4)-(Y(9)**4))
      TREACP=YDOT(4)*DELHP*3.7475/231.54

      IF(IMELT2.NE.1)FES=Y(4)
      IF(IMELT2.EQ.1)YMELT=-(Y(4)-FES)*DELHP*3.7475/231.54
      IF(IMELT2.EQ.1)YMELT=YMELT+PMASS*81.538

      YDOT(9)=(PARECM*(CONVTP+RADTP)+TREACP)/(CPp*PMASS)

      CCCCCC BALANCE ON LIQUID IRON OXIDE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      IF(STEMP.LT.TCRYST)YDOT(10)=0.0
      IF(IOXIDE.NE.1)GOTO 11
      YDOT(10)=AKD*PYRO*AREA(1)-(GCON*AFEL/(CAREA-AFEL))
      IF(STEMP.LT.TCRYST)YDOT(10)=0.0
11      CONTINUE

      RETURN
      END

      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      CCCCCC SUBROUTINE TO DETERMINE REACTION RATE JACOBIAN CCCCCCCCCCCCCCCCCC
      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      SUBROUTINE JAC(NEQ,T,Y,B)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(50),B(50,50),CON(25)
      DIMENSION AREA(8),RAD(3),CMASS(2)
      INCLUDE 'MODCON.COM'

      CCCCCC INITIALIZE JACOBIAN TO ZERO CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      DO 1 I=1,50

```



```

      DO 2 J=1,50
        B(I,J)=0.0
2      CONTINUE
1      CONTINUE

CCCCCC DETERMINE TEMPERATURE, PO2, AND PYRITE-SILICATE MASS CCCCCCCCCC

      CALL TEMP(T,CTEMP)

      TOP=1-(Y(1)/CHAR0)
      BOTT=1-(ASHMASS/CHAR0)
      CX=TOP/BOTT

      STEMP=Y(5)
      PTEMP=Y(9)

      CALL PYRITE(Y,STEMP,PYRO)
      CALL SIL(Y,STEMP,SIO2)
      ST=2000
      CALL SIL(Y,ST,SIO2B)

      WATER=(TOTCOAL*CON(21)/18)+(CX*TOTCOAL*CON(22)/36)
      TOTMOL=Y(6)+WATER+Y(7)+Y(8)+GMOLN2
      V=TOTMOL*82.06*CTEMP

      PO2=Y(6)/TOTMOL

CCCCCC DETERMINE CHAR OXIDATION CONST CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      R=1.987E-3
      PI=3.14159

      CHARK2=-CON(14)*EXP(-CON(13)/(STEMP*R))
      CHARK1=-CON(14)*EXP(-CON(13)/(CTEMP*R))
      CHARRAT=CHARK1/CHARK2
      C=(3/(1.5*4*PI))**0.66666666666666666666

CCCCCC GET DATA ON THE CHAR AND ASH CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      CALL DAT(PYRO,SIO2,Y,AREA,RAD,CMASS)          !GET ASH&CHAR INFO

      CAREA=AREA(6)
      CHRAD=RAD(1)

CCCCCC CALCULATE THE EFFICIENCY CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      CALL EFF(CTEMP,PO2,CHARK2,CHRAD,SPO2,STEMP)

CCCCCC CALCULATE CHAR BURNOUT JACOBIAN CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      IF(Y(1).LE.ASHMASS)Y(1)=ASHMASS
      IF(Y(1).LE.ASHMASS)GOTO 3

      IF(STEMP.LT.600)GOTO 3
      B(1,1)=(SPO2**0.5)*CHARK2*PI*C/(Y(1)**0.3333333)
      B(1,5)=CHARK2*CAREA*(SPO2**0.5)*(CON(13)/R)/(STEMP**2)
3      CONTINUE

```

CCCCCCC DETERMINE ASH COMPONENT AREAS CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

FEL=0.0
IF((IOXIDE.EQ.1).AND.(STEMP.GT.1600))FEL=Y(10)

RHOG=(GF*2.5+5)/(1+GF)
DG3=(1/RHOG)*(1/(1+GF))*(2.5*(CON(17)**3)*GF+5.0*(CON(18)**3))
DG=DG3**0.333333333

AG=6/(4*RHOG*DG)
AP=6/(4*CON(18)*5.0)
AS=6/(4*CON(17)*2.5)
AS2=AS*4

AREAI=AP*(PYRO+FEL)

AREAASH=(Y(3)+PYRO+Y(10))*AP+(Y(2))*AG+SIO2B*AS

IF(Y(1).LE.ASHMASS)CAREA=AREAASH
IF(Y(1).LE.ASHMASS)CHRAD=(AREAASH/(4*3.14159))**0.5

AFEL=FEL*AP

CB=-TOTCOAL/BOTT

```

CCCCCCC DETERMINE GLASS FORMATION JACOBIAN CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

IF(CAREA.GT.AREAASH)X2=AREAI/(CAREA-AREAI)
IF(CAREA.LE.AREAASH)X2=AREAI/(AREAASH-AREAI)

GCON=GK*SIO2*AS2*EXP(-EG/STEMP)

B(2,1)= CON(6)*GK*AS2*X2*CB*EXP(-EG/STEMP)
B(2,2)=- (GK*AS2*X2*GF/(1+GF))*EXP(-EG/STEMP)
B(2,5)= X2*GCON*EG/(STEMP**2)

```

CCCCCCCCC COMPUTE THE DIFFUSIVITY OF OXYGEN CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

TMEAN=(STEMP+CTEMP)/2
DIFF=2.4*((TMEAN/1800)**1.75)

```

CCCCCCC DETERMINE IRON OXIDATION JACOBIAN CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

C-----FOR LIQUID PYRRHOTITE -----C

```

AKoc=2*DIFF/CON(18)

IF(STEMP.GT.1356)AKic=0.75*AKoc      !From Srinivasachar
IF(STEMP.LE.1356)AKic=0.30*AKoc    !From Srinivasachar
IF(STEMP.LT.600)GOTO 13

IF(IMELT.NE.1)GOTO 6
AKtot=1/((1/AKoc)+(1/AKic))
AKD=61.78*AKtot*SPO2/(82.06*CTEMP)

B(3,1)=AKD*AREA(1)*CB*CON(7)
B(3,2)=-AKD*AREA(1)/(GF+1)
B(3,3)=-AKD*AREA(1)/0.827

```

6 CONTINUE

C----- FOR SOLID PYRRHOTITE -----C

```

FEK=5E9*EXP(-18042/STEMP)
AK=1/((1/AKoc)+(1/AKic)+(1/FEK))
AKD=61.78*AK*SPO2/(82.06*CTEMP)
IF(IMELT.EQ.1)GOTO 7
  B(3,1)=AKD*AREA(1)*CB*CON(7)
  B(3,2)=-AKD*AREA(1)/(GF+1)
  B(3,3)=-AKD*AREA(1)/0.827
  B(3,10)=-AKD*AREA(1)/0.827
7  CONTINUE
   GOTO 13

```

CCCCCCC DETERMINE OXIDATION RATE OF EXTRANEIOUS MATERIAL CCCCCCCCCCCCCC

```

PRAD=CON(11)/2.0
PARE=4*3.14159*(PRAD**2)
PRADCM=PRAD*100
PARECM=4*3.14159*(PRADCM**2)
PTMEAN=(PTEMP+CTEMP)/2

PMASS=4*3.14159*(PRADCM**3)*5.0/3
PYROHIT=PMASS-(Y(4)/0.827)
IF(PYROHIT .LE. 0.0)PYROHIT=0.0
IF(PYROHIT .EQ. 0.0)GOTO 9
IF(PTEMP.LT.600)GOTO 9

DIFFPY=2.4*((PTMEAN/1800)**1.75)

AKo=DIFFpy/(PRADCM) !Gas Phase Mass Trans. (cm/sec)
IF(PTEMP.GT.1356)AKi=0.75*AKo
IF(PTEMP.LE.1356)AKi=0.30*AKo

```

C----- FOR LIQUID PYRRHOTITE -----C

```

IF(IMELT2 .NE. 1)GOTO 8
  AKt=1/((1/AKo)+(1/AKi))
  AKDP=61.784*AKt/(82.06*PTMEAN)
  B(4,6)=AKDP*PARECM/TOTMOL
8  CONTINUE

```

C----- FOR SOLID PYRRHOTITE -----C

```

IF(IMELT2 .EQ. 1)GOTO 9
  FEKE=EXP(-18042/PTEMP)*5e9
  AKt=1/((1/AKoc)+(1/AKic)+(1/FEKE))
  AKD=61.748*AKt*PO2/(82.06*CTEMP)
  B(4,6)=(AKD/PO2)*PARECM/TOTMOL
9  CONTINUE

```

CCCCCCC DETERMINE PARTICLE TEMPERATURE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

SIGMA=1.355E-12
EPS=0.8

CP=(4.03+0.00114*STEMP-(204000/(STEMP**2)))/12
TMEAN=(CTEMP+STEMP)/2

THERMK=5.7838E-5*((TMEAN/298)**.75)
CK=THERMK/CHRAD

```

```

WALLT=0.95*CTEMP
DELHC=(25428.+0.82*STEMP*0.00033*STEMP**2+(213000/STEMP))/12

B(5,1)=-B(1,1)*DELHC/(CP*Y(1))
B(5,5)=CAREA/(CP*Y(1))
B(5,5)=B(5,5)*((-THERMK/CHRAD)-4*SIGMA*EPS*(Y(5)**3))
B(5,5)=B(5,5)-B(1,5)/(CP*Y(1))

CCCCCCCC DETERMINE CONCENTRATIONS CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

CO2B=Y(6)/V          !BULK O2 CONC. (MOL/CC)
CCOB=Y(7)/V          !BULK CO CONC. (MOL/CC)
CCO2B=Y(8)/V         !BULK CO2 CONC. (MOL/CC)
CH2O=WATER/V         !BULK WATER CONC. (MOL/CC)

CCCCCCCCCCCC DETERMINE CO-CO2 TRANSFORMATION CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

RB=5.E8*V*EXP(-20130/CTEMP)*CCO2B
RF=3.9E14*V*EXP(-20130/CTEMP)*CCOB*(CH2O**0.5)*(CO2B**0.25)

AKCO=DIFF*36*3.14159*CHRAD/1000.

CCCCCCCCCCCC DETERMINE OXYGEN BALANCE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

B(6,1)=B(1,1)/24

CCCCCCCCCCCC CO BALANCE IN BULK CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

B(7,1)=B(1,1)/12

CCCCCCCC DETERMINE PYRITE TEMPERATURE JACOBIAN CCCCCCCCCCCCCCCCCCCCCCCCCC

SIGMA=1.355E-12
EPS=0.5
CPp=0.50
PTMEAN=(CTEMP+PTEMP)/2

THERMK=5.7838E-5*(PTMEAN/298)**0.75)
CKP=THERMK/PRADCM
WALLT=0.98*CTEMP
IF(IMELT2.EQ.1)DELHP=4.544E4
IF(IMELT2.NE.1)DELHP=4.810E4

B(9,9)=PARECM/(CPP*PMASS)
B(9,9)=B(9,9)*((-THERMK/PRADCM)-4*SIGMA*EPS*(Y(9)**3))
B(9,9)=B(9,9)-B(4,9)/(CPP*PMASS)

CCCCCCCC DETERMINE IRON OXIDATION JACOBIAN CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
IF(X2.EQ.0.0)GOTO 11
XL=AFEL/(CAREA-AFEL)
C-----FOR LIQUID PYRRHOTITE -----C
IF(IOXIDE.NE.1)GOTO 13
IF(STEMP.GT.TCRYST)GOTO 11
B(10,1)=-AKD*AREA(1)*CB*CON(7)-(B(2,1)*XL/X2)
B(10,2)=(-AKD*AREA(1)/(GF+1))-(B(2,2)*XL/X2)
B(10,3)=AKD*AREA(1)/0.827
B(10,5)=-B(2,5)*XL/X2
B(10,6)=AKD*PYRO*AREA(1)/TOTMOL

```

11 CONTINUE

```

      IF(STEMP.GT.1600)GOTO 13
      DO 12 I=1,11
        B(10,I)=0.0
12     CONTINUE
13     CONTINUE
      RETURN
      END

```

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCC SUBROUTINE TO DETERMINE DFDX OF THE SYSTEM CCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

```

      SUBROUTINE DFDX(NEQ,T,Y,ALP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(50),ALP(50,50)
      INCLUDE 'MODCON.COM'

      DO 13 I=1,50
        DO 14 J=1,50
          ALP(I,J)=0.0
14     CONTINUE
13     CONTINUE

      RETURN
      END

```

```

CCCCCCCCC SUBROUTINE TO SOLVE ODES CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

```

C
C   MODIFIED 2/11/91 TO BE USED INSTEAD OF LSODE
C
C   AUTHOR: J.O.L.WENDT, DEPT OF CHEM ENG, UNIV. ARIZONA
C
      SUBROUTINE TYSON (FUN,JAC,DFDX,N,Y,X,H,BUG1,BUG2,DELTA,IN)
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL FUN,JAC,DFDX
      DIMENSION Y(50),F(50)
      DIMENSION ALP(50),B(50,50),A(50,51),ASTORE(50,51)
      REAL*8 K(50),K1(50),KBY(50)
      DIMENSION ADASH(50,51)
      REAL*8 K1DASH(50)
      INTEGER BUG1,BUG2
      DIMENSION OLDY(50),OLDF(50),OLDALP(50),OLDB(50,50),OLDK1(50),BIGK(
150)
C
C   CALL FUN FOR VALUES OF F(I) (YDOT(I))
C   CALL JAC FOR JACOBIAN B(I,J), ( DF(I) OR DYDOT(I) BY DY(J) )
C   CALL DFDX FOR ALP(I), ( DF(I) OR DYDOT(I) BY DX,
C   FOR NON AUTONOMOUS SYSTEMS)
C
      CALL FUN (N,X,Y,F)
      CALL JAC (N,X,Y,B)
C   IF ( (F(3).NE.0.0).AND.(b(3,3).EQ.0.0) ) WRITE(*,*) 'ZERO'
      CALL DFDX (N,X,Y,ALP)
      IF(IN.NE.0) GO TO 1
      FACT=-1.0E-28
      IF (H.GT.1.) FACT=H
      IF (FACT.GT.0.) CALL STEPIN (N,H,B,FACT)
      IDEBUG=1

```

```

      ISTEP=0
      ITYSON=0
      IN=1
1    IF(IN.NE.1) GO TO 2
10   ITYSON=1+ITYSON
C
C     IMPLICIT EULER FOR FIRST STEP
C
      CALL EULIMP (N,Y,F,X,H,ALP,B,ASTORE,K,A)
C
C     SUCCESSFUL? TAKE A STEP
C
      CALL EULSTP (N,Y,K,H,KBY,Y,IFLAG,DELTA)
      CALL STORE (N,Y,F,X,H,ALP,B,K1,HP,IFLAG,
1OLDY,OLDF,OLDALP,OLDB,OLDK1,OLDHP,OLDX)
      IF(IFLAG.EQ.1) THEN
C      WRITE(*,1000)X,H,ISTEP,ITYSON
      WRITE(16,1000)X,H,ISTEP,ITYSON
1000  FORMAT(' STEP SIZE IS DECREASING AT TIME=',E10.3,'STEP=',E10.3,
1' ISTEP=',I3,'ITYSON=',I4)
      ENDIF
      IF (BUG1.EQ.0) GO TO 11
      IF (MOD(IDEBUG,BUG1).NE.0)
1CALL TYDBUG(N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBUG,
1ASTORE,K,K1,KBY,Y,HP,IFLAG,FACT,A,ISTEP,BIGK,OLDF,OLDALP,OLDB,OLDK1
1,OLDHP,ADASH,K1DASH,BIGH)
      IF (MOD(ITYSON,BUG2).EQ.0)
1CALL TYDBUG(N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBUG,
1ASTORE,K,K1,KBY,Y,HP,IFLAG,FACT,A,ISTEP,BIGK,OLDF,OLDALP,OLDB,OLDK1
1,OLDHP,ADASH,K1DASH,BIGH)
      IF(ITYSON.GE.10) THEN
        CLOSE(3,STATUS='KEEP')
        STOP
      ENDIF
11  IF (IFLAG.EQ.1) GO TO 10
      ISTEP =ISTEP+1
      CALL FORWAD (N,Y,F,X,H,K,K1,HP,IFLAG,K1DASH)
      IN =2
      RETURN
2  CONTINUE
      IFLAG=2
      ITYSON=ITYSON+1
      CALL TYSINT(N,Y,F,X,H,ALP,B,K,K1,HP,ASTORE,A)
      CALL CHECKY(N,Y,H,K,IFLAG)
      IF (IFLAG.EQ.1) GO TO 3
      NSTEP=ISTEP+1
      IF (MOD(NSTEP,2).EQ.0)
1CALL TYSTEP (N,Y,K,H,HP,X,K1,OLDY,OLDF,OLDALP,OLDB,OLDK1,OLDHP,
1BIGK,IFLAG,NSTEP,KBY,Y,DELTA,ADASH,A,BIGH,K1DASH)
      IF (MOD(ISTEP,2).NE.0) GO TO 3
      IF (IFLAG.EQ.1) GO TO 3
      CALL STORE (N,Y,F,X,H,ALP,B,K1,HP,IFLAG,
1OLDY,OLDF,OLDALP,OLDB,OLDK1,OLDHP,OLDX)
3  CONTINUE
      IF(IFLAG.EQ.1)THEN
C      WRITE(*,1000)X,H,ISTEP,ITYSON
      WRITE(16,1000)X,H,ISTEP,ITYSON
      ENDIF
      IF (BUG1.EQ.0) GO TO 12
      IF(MOD(IDEBUG,BUG1).NE.0)
1CALL TYDBUG(N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBUG,

```

```

1ASTORE,K,K1,KBY,Y,HP,IFLAG,FACT,A,ISTEP,BIGK,OLDF,OLDALP,OLDB,OLDK1
1,OLDHP,ADASH,K1DASH,BIGH)
  IF (MOD(ITYSON,BUG2).EQ.0)
1CALL TYDBUG(N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBUG,
1ASTORE,K,K1,KBY,Y,HP,IFLAG,FACT,A,ISTEP,BIGK,OLDF,OLDALP,OLDB,OLDK1
1,OLDHP,ADASH,K1DASH,BIGH)
12 IF (IFLAG.EQ.1) GO TO 2
    ISTEP=ISTEP+1
    CALL FORWAD (N,Y,F,X,H,K,K1,HP,IFLAG,K1DASH)
    RETURN
  END
  SUBROUTINE FORWAD(N,Y,F,X,H,K,K1,HP,IFLAG,K1DASH)
  IMPLICIT REAL*8 (A-H,O-Z)
  REAL*8 K1DASH(50)
  DIMENSION Y(50),F(50)
    REAL*8 K(50),K1(50)
  DO 2 I=1,N
    Y(I)=Y(I)+K(I)
    K1DASH(I)=K1(I)
    K1(I)=K(I)
  2 CONTINUE
  X=X+H
  HP=H
  IF (IFLAG.GE.3) GO TO 1
  RETURN
1 CONTINUE
  IF (IFLAG.EQ.3) H=2.*H
  IF (IFLAG.EQ.4) H=4.*H
  IF (IFLAG.EQ.5) H=10.*H
  IF (IFLAG.EQ.6) H= 100.*H
  RETURN
  END
  SUBROUTINE EULSTP (N,Y,K,H,KBY,Y,IFLAG,DELTA)
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION Y(50)
    REAL*8 K(50),KBY(Y(50))
  IFLAG =2
  DO 2 I=1,N
    YNEW=Y(I)+K(I)
    IF(YNEW.LT.0.) IFLAG=1
  2 CONTINUE
  IF(IFLAG.NE.1) GO TO 3
  1 H=H/10.
  RETURN
  3 DO 5 I=1,N
    YNEW=Y(I)+K(I)
    IF (Y(I).LT.1.0D-14) GO TO 5
    KBY(Y(I))=ABS(K(I)/YNEW)
    IF (KBY(Y(I)).GT.DELTA*10.) IFLAG=1
  5 CONTINUE
  IF (IFLAG.EQ.1) H=H/10.
  RETURN
  END
  SUBROUTINE EULIMP(N,Y,F,X,H,ALP,B,ASTORE,K,A)
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION Y(50),F(50)
  REAL*8 K(50)
  REAL*8 K1(50)
  DIMENSION ALP(50),B(50,50),A(50,51),ASTORE(50,51)
  DIMENSION RHS(50),ANS(50),IPVT(50)
  1 DO 2 I=1,N

```

```

      DO 2 J=1,N
      A(I,J)=-H*B(I,J)
2    CONTINUE
      DO 3 I=1,N
      A(I,I)=1.-H*B(I,I)
      RHS(I)=H*(F(I)+H*ALP(I))
3    CONTINUE
      DO 4 I =1,N
      DO 5 J=1,N
5    ASTORE(I,J)=A(I,J)
4    ASTORE(I,N+1)=RHS(I)
      CALL LINPAC(N,A,RHS,ANS,IPVT)
      DO 7 I=1,N
      K(I)=ANS(I)
C      IF(DABS(K(I)).LT.1.0D-16)K(I)=0.D00
7    CONTINUE
      RETURN
      END
      SUBROUTINE VECTOR (NAME,ARRAY,COLUMN)
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*6 NAME
      INTEGER COLUMN
      DIMENSION ARRAY(COLUMN)
      IF (COLUMN.NE.0) GO TO 9000
      WRITE (3,8000) NAME
      GO TO 1
8000  FORMAT (1H ,10X,A6)
9000  CONTINUE
      WRITE (3,1000) NAME
1000  FORMAT (1H ,10X,A6,1X,6HVECTOR)
3000  FORMAT (6(2X,1PD10.3))
      WRITE (3,3000) (ARRAY(J),J=1,COLUMN)
1    CONTINUE
      RETURN
      END
      SUBROUTINE STEPIN (N,H,B,FACT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION B(50,50)
      B11=DABS(B(1,1))
      B12=DABS(B(1,2))
      BMAX=DMAX1(B11,B12)
      DO 1 I=1,N
      DO 1 J=1,N
      BIJ=DABS(B(I,J))
      BMAX=DMAX1(BMAX,BIJ)
1    CONTINUE
      CHATIM=1.D00/BMAX
      H=CHATIM/FACT
      RETURN
      END
      SUBROUTINE TYDEBUG (N,Y,F,X,H,ALP,B,BUG1,BUG2,DELTA,IN,ITYSON,IDEBU
1G,ASTORE,K,K1,KBY,Y,HP,IFLAG,FACT,A,ISTEP,BIGK,OLDF,OLDALP,OLDB,
1OLDK1,OLDHP,ADASH,K1DASH,BIGH)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(50),F(50)
      DIMENSION ALP(50),B(50,50),A(50,51),ASTORE(50,51)
      REAL*8 K(50),K1(50),KBY,Y(50)
      REAL*8 K1DASH(50)
      DIMENSION BIGK(50)
      REAL*8 OLDF(50),OLDALP(50),OLDB(50,50),OLDK1(50),ADASH(50,51)
      INTEGER ROW,COLUMN,BUG1,BUG2

```



```

      IDEBUG=IDEBUG+1
      WRITE(3,1000)
      WRITE(13,1000)
1000 FORMAT (1H0,10X,20HTYSON DEBUG PRINTOUT)
      CALL DBSNGI (' ISTEP',ISTEP)
      CALL DBSNGI (' ITYSON',ITYSON)
      CALL DBSNGI (' IDEBUG',IDEBUG)
      CALL DBSNGI (' IFLAG',IFLAG)
      CALL DBSNGI ('   IN',IN)
      CALL DBSNGE ('  FACT',FACT)
      CALL DBSNGE ('  DELTA',DELTA)
      CALL DBSNGE ('    H',H)
      CALL DBSNGE ('   HP',HP)
      CALL DBSNGE ('    X',X)
      CALL DBSNGI ('  BUG1',BUG1)
      CALL DBSNGI ('    N',N)
      CALL DBSNGI ('  BUG2',BUG2)
      COLUMN=N
      CALL VECTOR ('    Y',Y,COLUMN)
      CALL VECTOR ('    F',F,COLUMN)
      CALL VECTOR ('  ALP',ALP,COLUMN)
      CALL VECTOR ('    K',K,COLUMN)
      CALL VECTOR ('  K1',K1,COLUMN)
      CALL VECTOR ('  KBYY',KBYY,COLUMN)
      CALL VECTOR ('  BIGK ',BIGK,COLUMN)
      ROW=N
      NROW=50
      CALL MATRIX ('  BETA',B,ROW,COLUMN,NROW)
      COLUMN=N+1
      CALL MATRIX ('ASTORE',ASTORE,ROW,COLUMN,NROW)
C      NROW=50
C      CALL MATRIX ('    A',A,ROW,COLUMN,NROW)
C      CALL DBSNGE ('  BIG H',BIGH)
C      CALL DBSNGE ('OLD HP',OLDHP)
C      COLUMN=N
C      CALL VECTOR ('K1DASH',K1DASH,COLUMN)
C      CALL VECTOR ('  OLD F',OLDF,COLUMN)
C      CALL VECTOR ('OLD K1',OLDK1,COLUMN)
C      CALL VECTOR ('OLDALP',OLDALP,COLUMN)
C      ROW=N
C      NROW=50
C      CALL MATRIX ('  OLD B',OLDB,ROW,COLUMN,NROW)
C      COLUMN=N+1
C      CALL MATRIX ('  ADASH',ADASH,ROW,COLUMN,NROW)
      RETURN
      END
      SUBROUTINE TYSINT (N,Y,F,X,H,ALP,B,K,K1,HP,ASTORE,A)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(50),F(50),RHS(50),ANS(50),IPVT(50)
      DIMENSION ALP(50),B(50,50),A(50,51),ASTORE(50,51)
      REAL*8 K(50),K1(50)
      DO 1 I=1,N
      DO 1 J=1,N
      A(I,J)=-H*B(I,J)
1  CONTINUE
      DO 2 I=1,N
      IF((H+HP).EQ.0.0)WRITE(*,*)'h+hp',h,HP
      IF(HP.EQ.0.0)WRITE(*,*)'!!!!!! HP=0!!!!!!'
      A(I,I)=(HP+2.*H)/(H+HP)-H*B(I,I)
      RHS(I)=H*(F(I)+H*ALP(I))+K1(I)*H**2/(HP*(HP+H))
      A(I,N+1)=RHS(I)

```

```

2  CONTINUE
  DO 3 I=1,N
    DO 4 J=1,N
      4  ASTORE(I,J)=A(I,J)
      3  ASTORE(I,N+1)=A(I,N+1)
        CALL LINPAC(N,A,RHS,ANS,IPVT)
        DO 24 I=1,N
          K(I)=ANS(I)
C      IF(DABS(K(I)).LT.1.0D-16)K(I)=0.D00
24  CONTINUE
    RETURN
  END
  SUBROUTINE TYSTEP (N,Y,K,H,HP,X,K1,OLDY,OLDF,OLDALP,OLDB,OLDK1
1,OLDHP,BIGK,IFLAG,ISTEP,KBYY,DELTA,ASTORE,A,BIGH,KLDASH)
  IMPLICIT REAL*8 (A-H,O-Z)
    REAL*8 Y(50),K(50),K1(50)
    REAL*8 KBYY(50)
    REAL*8 KLDASH(50)
    REAL*8 OLDY(50),OLDF(50),OLDALP(50),OLDB(50,50),OLDK1(50),BIGK(50)
    REAL*8 ASTORE(50,51), A(50,51)
    IFLAG=2
    I1=0
    I2=0
    I3=0
    I4=0
    I5=0
    BIGH=H+HP
    IF (ISTEP.EQ.2)
      1CALL EULIMP (N,OLDY,OLDF,OLDX,BIGH,OLDALP,OLDB,ASTORE,BIGK,A)
    IF (ISTEP.GE.4)
      1CALL TYSINT(N,OLDY,OLDF,OLDX,BIGH,OLDALP,OLDB,BIGK,OLDK1,OLDHP
1,ASTORE,A)
    DO 1 I=1,N
      IF (DABS(OLDY(I)+BIGK(I)).LT.1.00D-16) GO TO 1
C
C      CHECKS STEP SIZE ONLY FOR SPECIES WITH APPRECIABLE ABSOLUTE
C      CHANGE
C
      DIFF=1.-DABS((OLDY(I)+BIGK(I))/(Y(I)+K(I)))
      KBYY(I)=DABS(DIFF)
      IF (KBYY(I).GE.0.001D00*DELTA) I5=1
      IF (KBYY(I).GE.0.01D00*DELTA) I4=1
      IF (KBYY(I).GE.0.1D00*DELTA) I3=1
      IF (KBYY(I).GE.DELTA) I1=1
      IF (KBYY(I).GE.10.D00*DELTA) I2=1
1  CONTINUE
      IF (I2.EQ.1) IFLAG=1
      IF (I2.NE.1.AND.I1.EQ.1) IFLAG=2
      IF (I1.NE.1) IFLAG =3
      IF (I3.NE.1) IFLAG=4
      IF (I4.NE.1) IFLAG=5
      IF (I5.NE.1) IFLAG=6
      IF (IFLAG.EQ.1) H=H/2.
      RETURN
    END
    SUBROUTINE DBSNGE (NAME,VALUE)
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*6 NAME
      WRITE (3,1000) NAME ,VALUE
      WRITE (13,1000) NAME ,VALUE
1000  FORMAT (1H ,5X,A6,2X,1H=,1PD13.6)

```

```

      RETURN
    END
    SUBROUTINE DBSNGI (NAME, IVALUE)
      IMPLICIT REAL*8 (A-H, O-Z)
      CHARACTER*6 NAME
      WRITE (3, 1000) NAME, IVALUE
      WRITE (13, 1000) NAME, IVALUE
1000  FORMAT (1H , 5X, A6, 1H=, I7)
      RETURN
    END
    SUBROUTINE MATRIX (NAME, ARRAY, ROW, COLUMN, NROW)
      IMPLICIT REAL*8 (A-H, O-Z)
      CHARACTER*6 NAME
      INTEGER ROW, COLUMN
      DIMENSION ARRAY(NROW, COLUMN)
1000  FORMAT (1H , 10X, A6, 1X, 6HMATRIX)
3000  FORMAT (6(2X, 1PD10.3))
      IF (NROW.EQ.0.OR.ROW.EQ.0.OR.COLUMN.EQ.0) GO TO 9999
      WRITE (13, 1000) NAME
      DO 2000 I=1, ROW
2000  WRITE (13, 3000) (ARRAY(I, J), J=1, COLUMN)
      GO TO 8000
9999  CONTINUE
      WRITE (13, 9876) NAME
9876  FORMAT (1H , 10X, A6)
8000  CONTINUE
      RETURN
    END
    SUBROUTINE STORE (N, Y, F, X, H, ALP, B, K1, HP, IFLAG,
1OLDY, OLDF, OLDALP, OLDB, OLDK1, OLDHP, OLDX)
      IMPLICIT REAL*8 (A-H, O-Z)
      REAL*8 Y(50), F(50), ALP(50), B(50, 50), K1(50)
      REAL*8 OLDY(50), OLDF(50), OLDALP(50), OLDB(50, 50), OLDK1(50)
      DO 1 I=1, N
        OLDY(I)=Y(I)
        OLDF(I)=F(I)
        OLDALP(I)=ALP(I)
        OLDK1(I)=K1(I)
        DO 1 J=1, N
          OLDB(I, J)=B(I, J)
1      CONTINUE
        OLDHP=HP
        OLDX=X
      RETURN
    END
    SUBROUTINE CHECKY(N, Y, H, K, IFLAG)
      IMPLICIT REAL*8 (A-H, O-Z)
      DIMENSION Y(50)
      REAL*8 K(50)
      IFLAG=2
      DO 1 I=1, N
        YNEW= Y(I) +K(I)
        IF (YNEW.LT.0.) IFLAG=1
1      CONTINUE
      IF(IFLAG.EQ.1) H=0.1*H
      RETURN
    END
    SUBROUTINE OVERFL(IFL)
      IFL=0
      RETURN
    END

```

```

SUBROUTINE LINPAC(N,A,B,X,IPVT)
DOUBLE PRECISION A(50,51),B(50),X(50)
DIMENSION IPVT(50)
CALL DGEFA(A,N,N,IPVT,INFO)
IF(INFO.NE.0)WRITE(6,20)
IF(INFO.NE.0)RETURN
20 FORMAT( 34H THE COEFFICIENT MATRIX IS SINGULAR)
CALL DGESL(A,N,N,IPVT,B,0)
DO 30 I=1,N
30 X(I)=B(I)
RETURN
END
SUBROUTINE DGEFA(A,LDA,N,IPVT,INFO)
INTEGER LDA,N,IPVT(50),INFO
DOUBLE PRECISION A(50,51)

```

DGEFA FACTORS A DOUBLE PRECISION MATRIX BY GAUSSIAN ELIMINATION.

ON ENTRY

A DOUBLE PRECISION(LDA, N)
THE MATRIX TO BE FACTORED.

LDA INTEGER
THE LEADING DIMENSION OF THE ARRAY A .

N INTEGER
THE ORDER OF THE MATRIX A .

ON RETURN

A AN UPPER TRIANGULAR MATRIX AND THE MULTIPLIERS
WHICH WERE USED TO OBTAIN IT.
THE FACTORIZATION CAN BE WRITTEN $A = L*U$ WHERE
L IS A PRODUCT OF PERMUTATION AND UNIT LOWER
TRIANGULAR MATRICES AND U IS UPPER TRIANGULAR.

IPVT INTEGER(N)
AN INTEGER VECTOR OF PIVOT INDICES.

INFO INTEGER
= 0 NORMAL VALUE.
= K IF $U(K,K) \leq 0.0$. THIS IS NOT AN ERROR
CONDITION FOR THIS SUBROUTINE, BUT IT DOES
INDICATE THAT DGESL OR DGED1 WILL DIVIDE BY ZERO
IF CALLED. USE RCOND IN DGEKO FOR A RELIABLE
INDICATION OF SINGULARITY.

LINPACK. THIS VERSION DATED 08/14/78 .
CLEVE MOLER, UNIVERSITY OF NEW MEXICO, ARGONNE NATIONAL LAB.

SUBROUTINES AND FUNCTIONS

BLAS DAXPY,DSCAL,IDAMAX

INTERNAL VARIABLES

DOUBLE PRECISION T
INTEGER IDAMAX,J,K,KP1,L,NM1

```

C
C      GAUSSIAN ELIMINATION WITH PARTIAL PIVOTING
C
      INFO = 0
      NM1 = N - 1
      IF (NM1 .LT. 1) GO TO 70
      DO 60 K = 1, NM1
        KP1 = K + 1
C
C        FIND L = PIVOT INDEX
C
        L = IDAMAX(N-K+1,A(K,K),1) + K - 1
        IPVT(K) = L
C
C        ZERO PIVOT IMPLIES THIS COLUMN ALREADY TRIANGULARIZED
C
        IF (A(L,K) .EQ. 0.0D0) GO TO 40
C
C        INTERCHANGE IF NECESSARY
C
        IF (L .EQ. K) GO TO 10
        T = A(L,K)
        A(L,K) = A(K,K)
        A(K,K) = T
10      CONTINUE
C
C        COMPUTE MULTIPLIERS
C
        T = -1.0D0/A(K,K)
        CALL DSCAL(N-K,T,A(K+1,K),1)
C
C        ROW ELIMINATION WITH COLUMN INDEXING
C
        DO 30 J = KP1, N
          T = A(L,J)
          IF (L .EQ. K) GO TO 20
          A(L,J) = A(K,J)
          A(K,J) = T
20        CONTINUE
          CALL DAXPY(N-K,T,A(K+1,K),1,A(K+1,J),1)
30      CONTINUE
        GO TO 50
40      CONTINUE
        INFO = K
50      CONTINUE
60 CONTINUE
70 CONTINUE
      IPVT(N) = N
      IF (A(N,N) .EQ. 0.0D0) INFO = N
      RETURN
      END
      SUBROUTINE DGESL(A,LDA,N,IPVT,B,JOB)
      INTEGER LDA,N,IPVT(50),JOB
      DOUBLE PRECISION A(50,51),B(50)
C
C      DGESL SOLVES THE DOUBLE PRECISION SYSTEM
C      A * X = B OR TRANS(A) * X = B
C      USING THE FACTORS COMPUTED BY DGECON OR DGEFA.
C
C      ON ENTRY

```

```

C      A      DOUBLE PRECISION(LDA, N)
C      THE OUTPUT FROM DGEKO OR DGEFA.
C
C      LDA     INTEGER
C      THE LEADING DIMENSION OF THE ARRAY  A .
C
C      N       INTEGER
C      THE ORDER OF THE MATRIX  A .
C
C      IPVT    INTEGER(N)
C      THE PIVOT VECTOR FROM DGEKO OR DGEFA.
C
C      B       DOUBLE PRECISION(N)
C      THE RIGHT HAND SIDE VECTOR.
C
C      JOB     INTEGER
C      = 0      TO SOLVE  A*X = B ,
C      = NONZERO TO SOLVE TRANS(A)*X = B WHERE
C                TRANS(A) IS THE TRANSPOSE.
C
C      ON RETURN
C
C      B       THE SOLUTION VECTOR  X .
C
C      ERROR CONDITION
C
C      A DIVISION BY ZERO WILL OCCUR IF THE INPUT FACTOR CONTAINS A
C      ZERO ON THE DIAGONAL.  TECHNICALLY THIS INDICATES SINGULARITY
C      BUT IT IS OFTEN CAUSED BY IMPROPER ARGUMENTS OR IMPROPER
C      SETTING OF LDA .  IT WILL NOT OCCUR IF THE SUBROUTINES ARE
C      CALLED CORRECTLY AND IF DGEKO HAS SET RCOND .GT. 0.0
C      OR DGEFA HAS SET INFO .EQ. 0 .
C
C      TO COMPUTE INVERSE(A) * C WHERE C IS A MATRIX
C      WITH P COLUMNS
C      CALL DGEKO(A,LDA,N,IPVT,RCOND,Z)
C      IF (RCOND IS TOO SMALL) GO TO ...
C      DO 10 J = 1, P
C      CALL DGESL(A,LDA,N,IPVT,C(1,J),0)
C      10 CONTINUE
C
C      LINPACK. THIS VERSION DATED 08/14/78 .
C      CLEVE MOLER, UNIVERSITY OF NEW MEXICO, ARGONNE NATIONAL LAB.
C
C      SUBROUTINES AND FUNCTIONS
C
C      BLAS DAXPY,DDOT
C
C      INTERNAL VARIABLES
C
C      DOUBLE PRECISION DDOT,T
C      INTEGER K,KB,L,NM1
C
C      NM1 = N - 1
C      IF (JOB .NE. 0) GO TO 50
C
C      JOB = 0 , SOLVE  A * X = B
C      FIRST SOLVE  L*Y = B
C
C      IF (NM1 .LT. 1) GO TO 30
C      DO 20 K = 1, NM1

```

```

        L = IPVT(K)
        T = B(L)
        IF (L .EQ. K) GO TO 10
        B(L) = B(K)
        B(K) = T
10      CONTINUE
        CALL DAXPY(N-K,T,A(K+1,K),1,B(K+1),1)
20      CONTINUE
30      CONTINUE
C
C      NOW SOLVE U*X = Y
C
        DO 40 KB = 1, N
            K = N + 1 - KB
            B(K) = B(K)/A(K,K)
            T = -B(K)
            CALL DAXPY(K-1,T,A(1,K),1,B(1),1)
40      CONTINUE
        GO TO 100
50      CONTINUE
C
C      JOB = NONZERO, SOLVE TRANS(A) * X = B
C      FIRST SOLVE TRANS(U)*Y = B
C
        DO 60 K = 1, N
            T = DDOT(K-1,A(1,K),1,B(1),1)
            B(K) = (B(K) - T)/A(K,K)
60      CONTINUE
C
C      NOW SOLVE TRANS(L)*X = Y
C
        IF (NM1 .LT. 1) GO TO 90
        DO 80 KB = 1, NM1
            K = N - KB
            B(K) = B(K) + DDOT(N-K,A(K+1,K),1,B(K+1),1)
            L = IPVT(K)
            IF (L .EQ. K) GO TO 70
            T = B(L)
            B(L) = B(K)
            B(K) = T
70      CONTINUE
80      CONTINUE
90      CONTINUE
100     CONTINUE
        RETURN
        END
        SUBROUTINE DAXPY(N,DA,DX,INCX,DY,INCY)
C
C      CONSTANT TIMES A VECTOR PLUS A VECTOR.
C      USES UNROLLED LOOPS FOR INCREMENTS EQUAL TO ONE.
C      JACK DONGARRA, LINPACK, 3/11/78.
C
        DOUBLE PRECISION DX(1),DY(1),DA
        INTEGER I,INCX,INCY,IX,IY,M,MP1,N
C
        IF(N.LE.0)RETURN
        IF (DA .EQ. 0.0D0) RETURN
        IF(INCX.EQ.1.AND.INCY.EQ.1)GO TO 20
C
C      CODE FOR UNEQUAL INCREMENTS OR EQUAL INCREMENTS
C      NOT EQUAL TO 1

```

```

C
  IX = 1
  IY = 1
  IF(INCX.LT.0)IX = (-N+1)*INCX + 1
  IF(INCY.LT.0)IY = (-N+1)*INCY + 1
  DO 10 I = 1,N
    DY(IY) = DY(IY) + DA*DX(IX)
    IX = IX + INCX
    IY = IY + INCY
10 CONTINUE
  RETURN

C
C      CODE FOR BOTH INCREMENTS EQUAL TO 1
C
C      CLEAN-UP LOOP
C
20 M = MOD(N,4)
  IF( M .EQ. 0 ) GO TO 40
  DO 30 I = 1,M
    DY(I) = DY(I) + DA*DX(I)
30 CONTINUE
  IF( N .LT. 4 ) RETURN
40 MP1 = M + 1
  DO 50 I = MP1,N,4
    DY(I) = DY(I) + DA*DX(I)
    DY(I + 1) = DY(I + 1) + DA*DX(I + 1)
    DY(I + 2) = DY(I + 2) + DA*DX(I + 2)
    DY(I + 3) = DY(I + 3) + DA*DX(I + 3)
50 CONTINUE
  RETURN
  END
  SUBROUTINE DSCAL(N,DA,DX,INCX)

C
C      SCALES A VECTOR BY A CONSTANT.
C      USES UNROLLED LOOPS FOR INCREMENT EQUAL TO ONE.
C      JACK DONGARRA, LINPACK, 3/11/78.
C
  DOUBLE PRECISION DA,DX(1)
  INTEGER I,INCX,M,MP1,N,NINCX

C
  IF(N.LE.0)RETURN
  IF(INCX.EQ.1)GO TO 20

C
C      CODE FOR INCREMENT NOT EQUAL TO 1
C
  NINCX = N*INCX
  DO 10 I = 1,NINCX,INCX
    DX(I) = DA*DX(I)
10 CONTINUE
  RETURN

C
C      CODE FOR INCREMENT EQUAL TO 1
C
C      CLEAN-UP LOOP
C
20 M = MOD(N,5)
  IF( M .EQ. 0 ) GO TO 40
  DO 30 I = 1,M
    DX(I) = DA*DX(I)

```



```

30 CONTINUE
   IF( N .LT. 5 ) RETURN
40 MP1 = M + 1
   DO 50 I = MP1,N,5
      DX(I) = DA*DX(I)
      DX(I + 1) = DA*DX(I + 1)
      DX(I + 2) = DA*DX(I + 2)
      DX(I + 3) = DA*DX(I + 3)
      DX(I + 4) = DA*DX(I + 4)
50 CONTINUE
   RETURN
   END
   DOUBLE PRECISION FUNCTION DDOT(N,DX,INCX,DY,INCY)

C
C   FORMS THE DOT PRODUCT OF TWO VECTORS.
C   USES UNROLLED LOOPS FOR INCREMENTS EQUAL TO ONE.
C   JACK DONGARRA, LINPACK, 3/11/78.
C
   DOUBLE PRECISION DX(1),DY(1),DTEMP
   INTEGER I,INCX,INCY,IX,IY,M,MP1,N

C
   DDOT = 0.0D0
   DTEMP = 0.0D0
   IF(N.LE.0)RETURN
   IF(INCX.EQ.1.AND.INCY.EQ.1)GO TO 20

C
C   CODE FOR UNEQUAL INCREMENTS OR EQUAL INCREMENTS
C   NOT EQUAL TO 1
C
   IX = 1
   IY = 1
   IF(INCX.LT.0)IX = (-N+1)*INCX + 1
   IF(INCY.LT.0)IY = (-N+1)*INCY + 1
   DO 10 I = 1,N
      DTEMP = DTEMP + DX(IX)*DY(IY)
      IX = IX + INCX
      IY = IY + INCY
10 CONTINUE
   DDOT = DTEMP
   RETURN

C
C   CODE FOR BOTH INCREMENTS EQUAL TO 1
C
C   CLEAN-UP LOOP
C
20 M = MOD(N,5)
   IF( M .EQ. 0 ) GO TO 40
   DO 30 I = 1,M
      DTEMP = DTEMP + DX(I)*DY(I)
30 CONTINUE
   IF( N .LT. 5 ) GO TO 60
40 MP1 = M + 1
   DO 50 I = MP1,N,5
      DTEMP = DTEMP + DX(I)*DY(I) + DX(I + 1)*DY(I + 1) +
      * DX(I + 2)*DY(I + 2) + DX(I + 3)*DY(I + 3) + DX(I + 4)*DY(I + 4)
50 CONTINUE
60 DDOT = DTEMP
   RETURN
   END
   INTEGER FUNCTION IDAMAX(N,DX,INCX)

```

```

C
C   FINDS THE INDEX OF ELEMENT HAVING MAX. ABSOLUTE VALUE.
C   JACK DONGARRA, LINPACK, 3/11/78.
C

```

```

DOUBLE PRECISION DX(1),DMAX
INTEGER I,INCX,IX,N

```

```

C
  IDAMAX = 0
  IF( N .LT. 1 ) RETURN
  IDAMAX = 1
  IF(N.EQ.1)RETURN
  IF(INCX.EQ.1)GO TO 20

```

```

C
C   CODE FOR INCREMENT NOT EQUAL TO 1
C

```

```

  IX = 1
  DMAX = DABS(DX(1))
  IX = IX + INCX
  DO 10 I = 2,N
    IF(DABS(DX(IX)).LE.DMAX) GO TO 5
    IDAMAX = I
    DMAX = DABS(DX(IX))
  5   IX = IX + INCX
10  CONTINUE
  RETURN

```

```

C
C   CODE FOR INCREMENT EQUAL TO 1
C

```

```

20  DMAX = DABS(DX(1))
  DO 30 I = 2,N
    IF(DABS(DX(I)).LE.DMAX) GO TO 30
    IDAMAX = I
    DMAX = DABS(DX(I))
30  CONTINUE
  RETURN
  END

```

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCC SUBROUTINE TO DETERMINE THE COAL DATA CCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

```

SUBROUTINE COALDAT(IDCOAL,DAT,COALNAM)
IMPLICIT REAL*8 (A-H,O-Z)
CHARACTER*8 COALNAM
DIMENSION DAT(25)

```

```

IF (IDCOAL .EQ. 1)THEN
  DAT(1)=0.210      !FRACTION QUARTZ
  DAT(2)=0.0598     !G SIL/G COAL
  DAT(3)=0.0155     !G PYR/G COAL
  DAT(4)=0.686      !FRACTION C IN COAL(ASH & H2O FREE)
  DAT(5)=0.0094     !G EXTR. PYR/G COAL
  DAT(6)=50E-6      !SIZE EXTR. PYRITE (M)
  DAT(7)=6.927      !STOICH MASS AIR/MASS FUEL
  DAT(10)=1500.     !FREEZING POINT OF ASH
  COALNAM='B. LIG.'
  DAT(11)=0.433     !Cp (CAL/G K)
  DAT(12)=7.43E-4   !MM SIZE SILICATE (CM)
  DAT(13)=31.07E-4  !MM SIZE PYRITE (CM)
  DAT(14)=32.64E-6  !MASS MEAN CHAR SIZE (M)

```

```

    DAT(15)=1460.
    DAT(16)=0.309
    DAT(17)=0.293
    DAT(18)=0.096
    DAT(19)=0.302
    DAT(20)=0.029
    DAT(21)=0.020
    DAT(22)=0.240
    DAT(23)=0.000
    DAT(24)=10.7
    END IF

    IF (IDCOAL .EQ. 2) THEN
        DAT(1)=0.550
        DAT(2)=0.0369
        DAT(3)=0.0016
        DAT(4)=0.718
        DAT(5)=0.0003
        DAT(6)=50E-6
        DAT(7)=8.053
        DAT(10)=1364.
        COALNAM='E.B.'
        DAT(11)=0.312
        DAT(12)=7.63E-4
        DAT(13)=13.02E-4
        DAT(14)=29.83E-6
        DAT(15)=1504.
        DAT(16)=0.362
        DAT(17)=0.338
        DAT(18)=0.048
        DAT(19)=0.252
        DAT(20)=0.038
        DAT(21)=0.030
        DAT(22)=0.240
        DAT(23)=0.000
        DAT(24)=5.46
    END IF

    IF (IDCOAL .EQ. 3) THEN
        DAT(1)=0.140
        DAT(2)=0.1463
        DAT(3)=0.0359
        DAT(4)=0.847
        DAT(5)=0.0059
        DAT(6)=50E-6
        DAT(7)=8.776
        DAT(10)=1465
        COALNAM='UF'
        DAT(11)=0.335
        DAT(12)=17.4E-4
        DAT(13)=31.6E-4
        DAT(14)=26.57E-6
        DAT(15)=1594.
        DAT(16)=0.523
        DAT(17)=0.240
        DAT(18)=0.232
        DAT(19)=0.005
        DAT(20)=0.041
        DAT(21)=0.480
        DAT(22)=0.280
        DAT(23)=0.110
    END IF

    !ASH FLUID TEMP (K)
    !FIXED CARBON (WT FRAC)
    !VOLATILES (WT FRAC)
    !ASH (WT FRAC)
    !MOISTURE (WT FRAC)
    !WT % H IN COAL
    !FRACTION ILLITE
    !FRACTION MIXED SILICATES
    !MF ORIGINAL FE IN SILICATE

    !FRACTION QUARTZ
    !G SIL/G COAL
    !G PYR/G COAL
    !FRACTION C IN COAL
    !G EXTR. PYR/G COAL
    !SIZE EXTR. PYRITE (M)
    !STOICH MASS AIR/MASS FUEL
    !FREEZING POINT OF ASH (K)

    !Cp (CAL/ G K)
    !MM SIZE SILICATE (CM)
    !MM SIZE PYRITE (CM)
    !MASS MEAN CHAR SIZE (M)
    !ASH FLUID TEMP (K)
    !FIXED CARBON (WT FRAC)
    !VOLATILES (WT FRAC)
    !ASH (WT FRAC)
    !MOISTURE (WT FRAC)
    !WT % H IN COAL
    !FRACTION ILLITE
    !FRACTION MIXED SILICATES
    !MF ORIGINAL IRON IN SILICATES

```

```

    DAT(24)=2.21
END IF

```

```

IF (IDCOAL .EQ. 4) THEN
    DAT(1)=0.160      !FRACTION QUARTZ
    DAT(2)=0.0924     !G SIL/G COAL
    DAT(3)=0.0156     !G PYR/G COAL
    DAT(4)=0.775      !FRACTION C IN COAL
    DAT(5)=0.0073     !G EXTR. PYR/G COAL
    DAT(6)=50E-6      !SIZE EXTR. PYRITE (M)
    DAT(7)=8.901      !STOICH MASS AIR/MASS FUEL
    DAT(10)=1479      !FREEZING POINT OF ASH
    COALNAM='KENT 9'
    DAT(11)=0.349      !Cp (CAL/G K)
    DAT(12)=5.93E-4   !MM SIZE SILICATE (CM)
    DAT(13)=7.77E-4   !MM SIZE PYRITE (CM)
    DAT(14)=24.6E-6   !MASS MEAN CHAR SIZE (M)
    DAT(15)=1495      !ASH FLUID TEMP (K)
    DAT(16)=0.429     !FIXED CARBON (WT FRAC)
    DAT(17)=0.345     !VOLATILES (WT FRAC)
    DAT(18)=0.143     !ASH (WT FRAC)
    DAT(19)=0.083     !MOISTURE (WT FRAC)
    DAT(20)=0.043     !WT % H IN COAL
    DAT(21)=0.310     !FRACTION ILLITE
    DAT(22)=0.450     !FRACTION MIXED SILICATES
    DAT(23)=0.000     !MF ORIGINAL FE IN SILICATES
    DAT(24)=2.47
END IF

```

```

IF (IDCOAL .EQ. 6) THEN
    DAT(1)=0.280      !FRACTION QUARTZ
    DAT(2)=0.1174     !G SIL/G COAL
    DAT(3)=0.0344     !G PYR/G COAL
    DAT(4)=0.768      !FRACTION C IN COAL
    DAT(5)=0.0143     !G EXTR. PYR/G COAL
    DAT(6)=50E-6      !SIZE EXTR. PYRITE (M)
    DAT(7)=8.710      !STOICH MASS AIR/MASS FUEL
    DAT(10)=1489.     !FREEZING POINT OF ASH
    COALNAM='K11'
    DAT(11)=0.349      !Cp (CAL/G K)
    DAT(12)=6.20E-4   !MM SIZE SILICATE (CM)
    DAT(13)=17.5E-4   !MM SIZE PYRITE (CM)
    DAT(14)=26.52E-6  !MASS MEAN CHAR SIZE (M)
    DAT(15)=1489.     !ASH FLUID TEMP (K)
    DAT(16)=0.419     !FIXED CARBON (WT FRAC)
    DAT(17)=0.338     !VOLATILES (WT FRAC)
    DAT(18)=0.203     !ASH (WT FRAC)
    DAT(19)=0.040     !MOISTURE (WT FRAC)
    DAT(20)=0.044     !WT % H IN COAL
    DAT(21)=0.240     !FRACTION ILLITE
    DAT(22)=0.350     !FRACTION MIXED SILICATES
    DAT(23)=0.030     !MF ORIGINAL FE IN SILICATES
    DAT(24)=2.05
END IF

```

```

IF (IDCOAL .EQ. 7) THEN
    DAT(1)=0.370      !FRACTION QUARTZ
    DAT(2)=0.0358     !G SIL/G COAL
    DAT(3)=0.0145     !G PYRITE/G COAL
    DAT(4)=0.777      !FRACTION C IN COAL
    DAT(5)=0.0096     !G EXTR. PYR/G COAL

```

```

    DAT(6)=50E-6          !SIZE EXTR. PYRITE (M)
    DAT(7)=8.984          !STOICH MASS AIR/MASS FUEL
    DAT(10)=1511          !FREEZING POINT OF ASH
    COALNAM='ILL6'
    DAT(11)=0.328         !Cp (CAL/G K)
    DAT(12)=3.4E-4        !MM SIZE SILICATE (CM)
    DAT(13)=11.0E-4       !MM SIZE PYRITE (CM)
    DAT(14)=21.93E-6      !MASS MEAN CHAR SIZE (M)
    DAT(15)=1489          !ASH FLUID TEMP (K)
    DAT(16)=0.422         !FIXED CARBON (WT FRAC)
    DAT(17)=0.359         !VOLATILES (WT FRAC)
    DAT(18)=0.086         !ASH (WT FRAC)
    DAT(19)=0.133         !MOISTURE (WT FRAC)
    DAT(20)=0.046         !WT % H IN COAL
    DAT(21)=0.190         !FRACTION ILLITE
    DAT(22)=0.330         !FRACTION MIXED SILICATES
    DAT(23)=0.000         !MF ORIGINAL FE IN SILICATES
    DAT(24)=1.97
  END IF

  DAT(8)=-5.94+0.355*DAT(4)*100
  ATM=2.8-0.0758*DAT(4)*100
  ALN=ATM+(DAT(8)/(1.987E-3*1750))
  DAT(9)=EXP(ALN)
  RETURN
END

```

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CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCC SUBROUTINE TO DETERMINE AREAS AND SIZES CCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

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```

SUBROUTINE DAT(PYRO,SIO2,Y,AREA,RAD,CMASS)
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION CON(25),Y(50)
  DIMENSION AREA(8),RAD(3),CMASS(2)
  INCLUDE 'MODCON.COM'

```

```

CCCCCCC CALCULATE ASHMASS AND COAL MASS CCCCCCCCCCCCCCCCCCCCCC

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```

    CMASS(1)=TOTCOAL*(CON(6)+CON(7))          !ASH MASS (G)
    CMASS(2)=CMASS(1)+Y(1)                    !COAL MASS (G)

```

```

    IF(Y(1).LE.ASHMASS)Y(1)=ASHMASS
    TOP=1-(Y(1)/CHARO)
    BOTT=1-(ASHMASS/CHARO)
    CX=1-(TOP/BOTT)

```

```

    CARBMAS=CHARO*CX

```

```

CCCCCCC CALCULATE ASH AND COAL RADIUS CCCCCCCCCCCCCCCCCCCCCC

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```

    PI=3.14159
    RHO=1.5
    R=1.987E-3

```

```

    RAD(1)=(CARBMAS*3/(RHO*4.0*PI))**0.333      !COAL RAD (CM)
    RAD(2)=((3*CMASS(1))/(4*PI*2.5))**0.333    !ASH RAD (CM)
    crad=rad(1)
    arad=rad(2)

```

```

RAD(3)=RAD(1)
IF(RAD(2) .GT. RAD(1))RAD(3)=RAD(2)

CCCCCC CALCULATE AREAS OF ASH AND CHAR CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

PYAREA=(6./(5.*CON(18)))          !AREA(SQSM)/G PYRITE
PYAREAM=6./(5.E6*CON(18)*1E-2)    !AREA(SQM)/G PYRITE
SIAREA=(6./(2.5*CON(17)))         !AREA(SQCM)/SILICATE

AREA(1)=PYAREA                    !AREA(SQCM)/G PYRITE
AREA(2)=PYAREAM                  !AREA(SQM)/G PYRITE
AREA(3)=PYAREA                   !AREA(SQCM)/G OXIDE
AREA(4)=SIAREA                   !AREA(SQCM)/G SILICATE
AREA(5)=SIAREA                   !AREA(SQCM)/G GLASS
AREA(6)=4*PI*(RAD(1)**2)         !AREA(SQCM) OF CHAR
AREA(7)=4*PI*(RAD(2)**2)         !AREA(SQCM) OF ASH
AREA(8)=AREA(6)

IF(AREA(7) .GT. AREA(6))AREA(8)=AREA(7)

RETURN
END

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCC SUBROUTINE TO COMPUTE SURFACE PO2 CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

SUBROUTINE EFF(CTEMP,PO2,CHARK2,CHARRAD,SPO2,STEMP)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION Y(50),CON(25)
INCLUDE 'MODCON.COM'

CCCCCCCCCC COMPUTE THE DIFFUSIVITY OF OXYGEN CCCCCCCCCCCCCCCCCCCCCCCCCCCCC

TM=(STEMP+CTEMP)/2
DIFF=2.4*((TM/1800)**1.75)

CCCCCCCC COMPUTE SURFACE PO2 CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

IF(CHARRAD.LE.0.0)SPO2=PO2
IF(CHARRAD.LE.0.0)GOTO 10
AKD=DIFF*24/(82.06*CTEMP*CHARRAD)
A=AKD
B=-CHARK2
C=-AKD*PO2

DETSQ=((B**2)-4*A*C)
IF(DETSQ.LE.0.0)WRITE(*,*)'SPO2 DETERMINANT <0'
IF(DETSQ.LE.0.0)STOP
DET=((B**2)-4*A*C)**0.5
SPO2HALF=(-B+DET)/(2*A)
SPO2=SPO2HALF**2
SPO2P=SPO2
10 CONTINUE

RETURN
END

```

[illegible]

```

SUBROUTINE PYRITE(Y,CTEMP,PYRO)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION Y(50),CON(25)
INCLUDE 'MODCON.COM'

TOP=1.-(Y(1)/CHARO)
BOT=1.-(ASHMASS/CHARO)
CX=(TOP/BOT)*TOTCOAL

PYRO=CX*CON(7)-(Y(2)/(GF+1))-((Y(3)+Y(10))/0.827)
IF(PYRO.LT.0.0)PYRO=0.0
IF(CTEMP.LT.600)PYRO=0.0

RETURN
END

```

[illegible]

```

SUBROUTINE SIL(Y,CTEMP,SIO2)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION Y(50),CON(25)
INCLUDE 'MODCON.COM'

TOP=1.-(Y(1)/CHARO)
BOT=1.-(ASHMASS/CHARO)
CX=(TOP/BOT)*TOTCOAL
SIO2B=CX*CON(6)-(GF*Y(2)/(GF+1))

XQ=CON(5)
XILL=CON(24)
XMISC=CON(25)
XKAO=1-XQ-XILL-XMISC

IF(CTEMP.GT.1258)SIO2=SIO2B*(1-XKAO)
IF(STEMP.GT.1650)SIO2=SIO2B
IF(CTEMP.LT.1258)SIO2=0.0

RETURN
END

```

[illegible]

```
SUBROUTINE TEMP(T,CTEMP)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION CON(25)
INCLUDE 'MODCON.COM'

TIME=T
AI=CON(1)
```

```

A2=CON(2)
B1=CON(3)
B2=CON(4)
CTEMP=A2*EXP(-A1*(TIME+B2))*(1-EXP(-B1*(TIME+B2)))

CTEMP=CTEMP+TOFFSET
IF(CTEMP.LT.298.0)CTEMP=298.0
RETURN
END

```

```

CCCCCCCCCCCC COMMON VARIABLES LIST CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
COMMON/CDATA/DENSCORR,CT2,CRITT,SR,GMOLN2
COMMON/COALS/CHAR0,TOTCOAL,ASHMASS,TOFFSET
COMMON/CONSTANT/CON
COMMON/FLAG/IT2,IT3,ITEMPFLAG
COMMON/OXY/SPO2P
COMMON/PLOTS/XG,AASH,AL,CARE
COMMON/test2/arad,crad
COMMON/CHECK/TCRYST,FES,IMELT,IMELT2,STMAX,IOXIDE
COMMON/GPARAM/GK,GF,EG,TRAN,TMELT,CHARRATE
COMMON/test3/YD1,YD2,YD3,TOPa,BOTa

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References Cited

- Abbot, M.F., Austin, L.G.; "Studies on Slag Deposit Formation in Pulverized-Coal Combustors"; *Fuel*, 64, 1985
- Adams, R.B., and Pask, J.A.; "Fundamentals of Glass to Metal Bonding: VIII, Nature of Wetting and Adherence"; *J. Am. Ceram. Soc.*, 45, 1962
- Austin et al.; "Study of the Mineral Matter Distribution in Pulverized Fuel Coals with Respect to Slag Deposit Formation on Boiler Tubes", DOE/ET/10560-T1, 1980
- Austin et al.; "Study of the Mineral Matter Distribution in Pulverized Fuel Coals with Respect to Slag Deposit Formation on Boiler Tubes", DOE/PC/30199-T1, 1984
- Asaki, Z., Mori, S., Ikeda, M., and Kondo, Y.; "Oxidation of Pyrrhotite Particles Falling through a Vertical Tube"; *Met. Trans. B.*, 16b, 1985
- Bassham, E.A., PhD Disseration, Department of Chemical Engineering, University of Arizona, 1992
- Baxter, L.L., Mitchell, R.E.; "The Release of Iron During the Combustion of Illinois No. 6 Coal"; *Combustion and Flame*, 88, 1992
- Boni, A., et al.; "Transformations of Inorganic Coal Constituents in Combustion Systems"; Quarterly Report No. 4, U.S. Department of Energy Contract No. DE-AC22-86PC90751, Pittsburgh Energy Technology Center, Pittsburgh, PA, Oct. 1987
- Boni, A., et al.; "Transformations of Inorganic Coal Constituents in Combustion Systems"; Phase I Final Report, U.S. Department of Energy Contract No. DE-AC22-86PC90751, Pittsburgh Energy Technology Center, Pittsburgh, PA, March 1990
- Boni, A., et al.; "Transformations of Inorganic Coal Constituents in Combustion Systems"; Quarterly Report No. 19, U.S. Department of Energy Contract No. DE-AC22-86PC90751, Pittsburgh Energy Technology Center, Pittsburgh, PA, Sept. 1991
- Boni, A., et al.; "Transformations of Inorganic Coal Constituents in Combustion Systems"; Phase II Final Report, U.S. Department of Energy Contract No. DE-AC22-86PC90751, Pittsburgh Energy Technology Center, Pittsburgh, PA, 1992
- Borio, R.W., Plumley, A.L. Sylvester, W.R.; "Improved Thermal Efficiency by Control of Factors Affecting Metal Wasteage in Pulverized Coal Fired Steam Generators"; *Ash Deposits and Corrosion Due to Impurities in Combustion Gasses*, McGraw-Hill, New York, New York, 1977

Borio, R.W., Narcisso Jr., R.R.; "The Use of Gravity Fractionation Techniques for Assessing Slagging and Fouling Potential of Coal Ash", *J. Eng. Power*, 101, 1979

Borio, R.W., Levasseur, A.A.; "Coal Ash Deposition in Boilers"; *Mineral Matter and Ash in Coal*, American Chemical Society, 1986

Bose, A.C.; "Pulverized Coal Combustion: Fuel Nitrogen Mechanisms in the Rich Post-Flame"; PhD Dissertation, Department of Chemical Engineering, University of Arizona, 1989

Brink, H.M., Eenkhoorn, S., Hamburg, G; "Mineral Transformations in Air-Staged Combustion of Pulverized Coal"; Report No. ECN-R-92-008, Netherlands Energy Research Foundation ECN, Petten, The Netherlands, 1992

Bryers, R.W.; "Influence of the Distribution of Mineral Matter in Coal in Fireside Ash Deposition"; *J. Eng. Power*, 101, 1979

Dryer, F.L., and Glassman, I. ; "High Temperature Oxidation of CO and CH₄"; *Fourteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1973

Duzy, A.F.; "Fusibility of Lignite Type Ash", ASME Paper 65-WA/FU-7 (as cited by Raask, 1985)

Duzy, A.F., and Walker, J.B.; "Utilization of Solid Fuels Having Lignite Type Ash", U.S. Bureau of Mines, Inf. Circ. 8304 (as cited by Raask, 1985)

French, D.N.; *Metallurgical Failures in Fossil Fired Boilers*, John Wiley & Sons, New York, New York, 1983

Frenkel, J.J.; "Viscous Flow of Crystalline Bodies Under the Action of Surface Tension"; *Jour. Phys. (Moscow)*, 2, 1945 (as cited by Raask, 1985, Kuczynski and Zaplatynskyj, 1956)

Gallagher, N.B.; "Alkali Metal Partitioning in Ash from Pulverized Coal Combustion"; PhD Dissertation, Department of Chemical Engineering, University of Arizona, 1992

Ghani, M.U.; "Early Evolution of Coal Nitrogen in Opposed Flow Combustion Configurations"; PhD Dissertation, Department of Chemical Engineering, University of Arizona, 1989

Gray, R.J., Moore, G.F. "Burning the Sub-Bituminous Coals of Montana and Wyoming in Large Utility Boilers", ASME Paper 74-WA/FU-1, 1974 (as cited by Raask, 1985)

Groves, S.J., Williamson, J., and Sanyal, A.; "Decomposition of Pyrite During Pulverized Coal Combustion", *FUEL*, 66, 1987

Hinds, W.C.; *Aerosol Technology*, John Wiley & Sons, 1982

Huffman, G.P., Huggins, F.E., Levasseur, A.A., Chow, O., Srinivasachar, S., and Mehta, A.A.; "Investigation of the Transformations of Pyrite in a Drop-Tube Furnace"; *Fuel*, 68, 1989

Hurt, R.H. and Hardesty, D.R., "The Rates and Mechanisms of Coal Char Combustion", Coal Combustion Science Quarterly Progress Report Oct-Dec 1991, Sandia Report SAND92-8211 UC-362, 1992

Hurt, R.H., and Mitchell, R.E.; "Unified High-Temperature Char Combustion Kinetics for a Suite of Coals of Various Rank"; *The Twenty Fourth International Symposium on Combustion*; Sidney, Australia, June 5-10, 1992

Hurt, R.H. and Mitchell, R.E.; "On the Combustion Kinetics of Heterogeneous Char Particle Populations"; *The Twenty Fourth International Symposium on Combustion*; Sidney, Australia, June 5-10, 1992

Jorgensen, F.R.A.; "On Maximum Temperatures Attained During Single Particle Combustion of Pyrite"; *Trans. Inst. Min. Metall.*; 90, 1981a

Jorgensen, F.R.A.; "Combustion of Pyrite Concentrate Under Simulated Flash-Smelting Conditions"; *Trans. Inst. Min. Metall.*; 90, 1981b

Kalamanovitch, D.P., Sanyal, A., Williamson, J.; "Slagging in Boiler Furnaces-a Prediction Technique Based on High Temperature Phase Equilibria"; *J. Inst. Energy*, 20, 1986

Kuczynski, G.C.; "Study of the Sintering of Glass"; *Jour. Appl. Phys.*, 20, 1949

Kuczynski, G.C., Zaplatynskyj, I.; "Sintering of Glass", *J. Am. Ceram. Soc.*, 56, 1956

Linak, W.P.; "The Effect of Coal Type, Residence Time and Combustion Configuration on the Submicron Aerosol Composition and Size Distribution from Pulverized Coal Combustion"; PhD Dissertation, Department of Chemical Engineering, University of Arizona, 1989

Lodge, J.P. Jr, Chan. Y.L., *Cascade Impactor: Sampling & Data Analysis*, American Industrial Hygiene Assoc., 1986

Marple, V.A., and Willeke, K; "Impactor Design", *Atmospheric Environment*, 10, 1976

Mereb, J.B.; "Nitrogen Oxide Abatement by Distributed Fuel Addition"; PhD Dissertation, Department of Chemical Engineering, University of Arizona, 1991

Metals Handbook, Ninth Edition, Vol. 11, "Failure Analysis and Prevention", American Society for Metals, 1986

Nowak, J.W., Benson, S.A., Jones, M.L., Kalmanovitch, D.P.; "Sintering Behavior and Strength Development in Various Coal Ashes"; *Fuel*, 69, 1990

Plumbridge, W.J.; "Metallography of High Temperature Fatigue"; *High Temperature Fatigue: Properties and Prediction*, Elsevier Science Publishing Co., New York, New York, 1987

Raask, E.; *Mineral Impurities in Coal Combustion*; Hemisphere Publishing Corp., New York, 1985

Reid, W.T; *External Corrosion and Deposits*, Elsevier Science Publishing Co., New York, New York, 1977

Reid, W.T., and Cohen, P.; "Factors Affecting the Thickness of Coal-Ash Slag on Furnace Wall Tubes"; *Trans. ASME*, 66, 1944

Richter, W, Payne, R., Heap, M.P.; "Influence of Thermal Properties of Wall Deposits on Performance of Pulverized Fuel Fired Boiler Combustion Chambers", *Mineral Matter and Ash In Coal*, American Chemical Society, 1986

Scotto, M.V., Bassham, E.A., Wendt, J.O.L., and Peterson, T.W.; "Quench Induced Nucleation of Ash Constituents during Combustion of Pulverized Coal in a Laboratory Furnace", *The Twenty Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburg, PA, 1989

Scotto, M.V.; "Mechanism Governing the Abatement of Metal Emissions from Waste Incineration"; PhD Dissertation, Department of Chemical Engineering, University of Arizona, 1992

Slag Atlas; Prepared by the Committee for Fundamental Metallurgy, Düsseldorf, Germany, 1981

Smith, I.W.; "Kinetics of Combustion of Size-Graded Pulverized Fuels in the Temperature Range 1200-2270 K"; *Combustion and Flame*, 17, 1971

Srinivasachar, S., and Boni, A. A., "A Kinetic Model for Pyrite Transformations in a Combustion Environment"; *FUEL*, 68, 1989

Thorpe, A.N., Senftle, F.E., Alexander, C., Dulong F.T., LaCount, R.B., and Friedman, S.; "Oxidation of Pyrite in an Anoxic Atmosphere", *FUEL*, 66, 1987

Turkdogan, E.T.; *Physicochemical Properties of Molten Slags and Glasses*; 1st Ed., The Metals Society, London, England, 1983

Westbrook, C.K., and Dryer, F.L.; "Simplified Reaction Mechanisms for the Oxidation of Hydrocarbon Fuels in Flames"; *Combust. Sci. Technol.*, 27, 1981

Vleeskens, J.M., Hamburg, G; "Depth of Combustion Inside Char from Evidence of Oxidized Pyrite", *Fuel*, 70, 1991

Vorres, K.S.; "Effect of Composition on Melting Behavior of Coal Ash"; *J. Eng. Power*, 101, 1979