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SECTIONS 6 AND 7

**TRANSFORMATIONS OF INORGANIC COAL
CONSTITUENTS IN COMBUSTION SYSTEMS**

Final Report

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SECTION 6

BEHAVIOR OF COAL INORGANIC SPECIES IN A LABORATORY SCALE PULVERIZED COAL COMBUSTOR (UA)

6. BEHAVIOR OF COAL INORGANIC SPECIES IN A LABORATORY SCALE PULVERIZED COAL COMBUSTOR (UA)

In this section of the report, results from an experimental investigation of the mechanisms governing the ash aerosol size segregated composition resulting from the combustion of pulverized coal in a laboratory scale down-flow combustor are described. The results of modeling activities used to interpret the results of the experiments conducted under this subtask are also described in this section. Although results from the entire program are included, Phase II studies which emphasized: 1) alkali behavior, including a study of the interrelationship between potassium vaporization and sodium vaporization; and 2) iron behavior, including an examination of the extent of iron-aluminosilicate interactions, are highlighted. Phase I baseline combustion experiments with the original suite of eight coals (see Section 3 of this report) have been described in detail in the Phase I Final Report (Boni et al., 1990).

The University of Arizona (UA) study was conducted in a self-sustained combustion down-flow laboratory furnace. This scale of experimentation was sufficiently large to allow pertinent phenomena in practical situations to be simulated, yet was also sufficiently small to allow the extraction of information about the relative importance of fundamental vaporization, condensation, and other physico-chemical mechanisms in determining the composition and size of the airborne ash. The seven coals examined during Phase I (Beulah Lignite, Eagle Butte, Kentucky #11, Kentucky #9, Upper Freeport, Illinois and Loy Yang 2301 (Australian)) and the four coals examined during Phase II (Illinois #6 SOAP, Eagle Butte/Kentucky #9 70/30 Blend, Loy Yang 1953, and Kentucky #9 Gravimelt-7A) were burned under overall fuel-lean conditions with the measured temperature histories being those which occurred naturally under those conditions. Special experiments in which temperature was varied by changing load and/or air preheat were subsequently performed on several coals, to help isolate composition and temperature effects. Selected experiments were also conducted with inorganic additives plus coal to evaluate certain aspects of the ash formation process.

In each run, effluent at the exhaust was extracted using a specially designed isokinetic, aspirated dilution probe. The sample was then passed through an Anderson Impactor and ash samples were collected to represent nine particle size cuts ranging from greater than 9 microns to less than $0.43\ \mu\text{m}$. Atomic absorption/emission spectroscopy yielded concentrations of aluminum, silicon, calcium, magnesium, iron, sodium, and potassium for each sample. Data from all runs consist of:

- a. Temperature profiles
- b. Ash composition in each nine size classes
- c. Total ash loading (as mg ash/sm^3 flue gas) in each of nine size classes, and
- d. For each element, the fraction of the original amount in the coal appearing in each of the nine size classes.

Data for each experiment is tabulated in Appendix 6.D.

6.1 Laboratory Scale Combustor

Experiments were conducted in a down-flow pulverized coal combustor. The insulated 17 kW (60,000 Btu/h) vertical combustor supported premixed and self-sustained flames of pulverized coal. This combustor (Figure 6.1-1) was designed to simulate the temperature histories and complex particle interactions of practical units, and yet yield a sufficiently well-characterized flow to allow for the study of fundamental rates and mechanisms. It has been in use for some time and is described in several other references (Bassham, 1992; Bose, 1989; Gallagher, 1992; Scotto, 1989). The plug-flow combustor, 6.1 m (20 ft) long, is a 15.2 cm (6 in.) ID tube constructed from sections of formed Zircar refractory and insulated with several inches of Kaowool insulation. The inlet of the furnace is comprised of a cone cast from Kaocrete refractory. In addition, approximately the first 2.7m (9 ft) of the furnace are lined with cast silicon carbide for durability. Sample ports, comprised of 5.1 cm (2 in.) mullite tubes, are placed along the length of the furnace for

FIGURE 6.1-1. - UA laboratory scale combustor.

temperature measurements and gas or particle extraction. 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 deg 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 the 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 any possible flash backs.

6.1.1 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 6.1-2. A pneumatically-driven vibrator was mounted to the side of the feeder bin to prevent bridging and channeling of coal. The coal was blown off the tip of the screw into the furnace by a metered stream of room temperature air. This

FIGURE 6.1-2. - Coal feeder

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 6.1-3). This natural gas (and air) flowrate was increased slowly over a period of 2 to 3 h to avoid thermal stress on the furnace. When the exhaust temperature was 400 to 500°C the gas was slowly turned off while the coal was turned on.

FIGURE 6.1-3. - Plenum section of furnace

6.1.2 Air Feed System

The air feed system for this furnace (Figure 6.1-4) 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 Speedaire compressor and filtered (three knockouts plus a backup filter) to remove oil and water before arriving at the appropriate section.

In the first section, the primary air, compressed air was passed through a regulator and a laminar flow meter at rates of 100 to 350 slpm. The metered flow was then passed through a 9 kW Chromalox electric air preheater where it was heated to the desired temperature (in most cases this was not used). From the preheater, the air passed through an insulated pipe to the mixing section above the plenum (Figure 6.1-5). In this section coal

FIGURE 6.1-4. - Air feed system

FIGURE 6.1-5. - Coal-air mixing section.

(and transport air) mixed with the primary air before entering the furnace. It was 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 section 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 20 to 80 slpm. However, in this case the air was passed directly to the coal feeder, bypassing the preheater. This air stream was never heated to avoid heating the coal prematurely, causing it to adhere to the screw. It was very important to observe the furnace when turning on the transport air. If the transport airflow was too high, coal was aspirated into the furnace and any feedrate control lost.

The last major segment of the air feed system was the UV purge air (10 to 15 slpm). 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.

6.1.3 Temperature Measurements

In each experiment a 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 12.7 mm (1/2 in.) O.D., 6.4 mm (1/4 in.) I.D. water cooled jacket, was inserted into the furnace at the desired ports. The thermocouple "bead" was extended approximately 6 mm beyond the end of the water cooled jacket for all measurements. The jacket was positioned so that the bead was centered within the furnace cross section for each measurement. 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.

6.1.4 Gas Sampling System

Combustion was monitored by sampling combustion gases at sample port 12 of the combustor. Port 12 was approximately 4.5m (14.6 ft) down from the burner with residence times exceeding 2.5s and char burnout was expected to be complete. The gas sample probe was a 6.4 mm (1/4 in.) stainless tube jacketed for water cooling. Quench water was supplied by a 1.6 mm (1/16 in.) stainless tube inside the sample tube. Quench rates for this probe have not been determined.

After the gas passed through the probe (essentially a watercooled tube), it was drawn through a knock out system where the sample was cooled and the water and particles removed (Figure 6.1-6). This dry, particle free stream, was then 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, it was possible to control the coal feedrate. The exact 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.

FIGURE 6.1-6. - Gas sampling system.

6.1.5 Fly Ash Particle Sampling System

The particle sampling system, Figure 6.1-7, included an isokinetic probe, a Mark II Anderson Cascade Impactor, and the previously mentioned gas analysis system. Ash, drawn into the probe (Figure 6.1-8) as isokinetically as possible, was quenched at a calculated rate of 10^6 K/s 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

FIGURE 6.1-7. - Particle sampling system

FIGURE 6.1-8. - Particle sampling probe.

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.

Using this configuration, sampling continued until a significant reduction in gas flow rate through the impactor after-filter was observed. In instances where a large sample mass was required (for example, CCSEM and Mössbauer samples), the flow through the filter was controlled by opening a valve downstream of the filter.

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 6.1-1). Samples to be analyzed by Computer Controlled Scanning Electron Microscopy (CCSEM) and Mössbauer were collected with the full impactor (earlier samples), three size classifications, or as a total filter (see Figure 6.1-9). 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 impaction substrates were either ash-free 0.2 μm Flouropore filters (all runs up to run 64) or ash-free 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 (Lodge, 1986). PEG-600 was dissolved in chloroform and sprayed on the filter substrate; filters were only used after the chloroform had evaporated. For the samples collected for EDX-Auger analysis, 45 mm Hytex 0.25 μm silver membrane filters 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 filters.

TABLE 6.1-1. - 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

AA, Anger, and CCSEM/Mossbauer

C-1953

FIGURE 6.1-9. - Impactor configurations.

6.1.6 Fly Ash Analysis

Impactor samples collected on teflon filters were analyzed for seven major elemental ash species: Al, Si, Ca, Fe, Na, K, and Mg. Analysis was performed by atomic absorption/emission (AA) using a Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer. The technique for analysis was a modification of the method recommended by Perkin-Elmer. A summary of the analysis technique is given here with a more complete description given by Bassham (1992).

Collected fly ash samples were prepared for analysis by dissolving in an acid solution in polystyrene vials. Collected samples included fly ash, any collected unburned char, the teflon filter, and PEG-600 sprayed on the filters. Analysis of the teflon filters, PEG-600, and the polystyrene container showed no measurable quantities of elements of interest. The dissolving acid composition is shown in Table 6.1-2 with the composition of other solutions pertinent to the analysis.

Samples were dissolved in 15 ml ($\pm$ 0.05 ml) of dissolving acid. Dissolving was augmented by sonicating samples in an ultrasonic bath for approximately 5 min. Sonication time was limited so as not to heat the samples and cause excessive evaporation. After these samples were allowed to sit for 24 to 48 h they were again subjected to a short period in the ultrasonic bath. To tie up excess fluoride and reduce loss of volatile silicon hexafluoride, 15 ml of boric acid was pipetted in the dissolved sample.

TABLE 6.1-2 - Atomic absorption analysis solution compositions

Component	Dissolving Acid	Acid Blank	Dilution Acid	Boric Acid (56.6 g/l)
HCl (39%)	100 ml	-	-	-
HNO ₃ (70%)	100 ml	-	-	-
HF (49%)	300 ml	-	-	-
Deionized water	500 ml	-	150 ml	733 ml
Cs soln (2000 ppm)	-	150 ml	-	267 ml
Dissolving acid	-	200 ml	200 ml	-
Boric acid	-	450 ml (25 g/l)	450 ml (25 g/l)	56.6g (H ₃ BO ₃)

Standard solutions were prepared before burn 30 by adding the appropriate amount of solid to a liter of DI water with cesium nitrate as an electron donor. Compounds are listed in Table 6.1-3. To improve accuracy, standard solutions were purchased after burn 29 in concentrations of 1000 ppm and cesium nitrate was added so that all solutions had a similar matrix. Sample analysis was performed using standard AA procedures. Raw data are listed in Appendix F.

Additional impactor samples were obtained for analysis by techniques other than atomic absorbance. Collected samples were analyzed at the University of Kentucky using a variety of techniques including computer controlled scanning electron microscopy (CCSEM), Mössbauer analysis, X-ray absorption fine structure analysis (XAFS), and X-ray absorption near edge structure analysis (XANES) (Boni et al. (1989), Shah et al. (1991), Huffman and Huggins (1978, 1989), Huggins et al. (1982)). Prior to burn 47 these samples were collected in a full impactor configuration. After burn 46 samples were collected on only plate 1, plate 4, and the after-filter. The abbreviated sampling procedure increased sample sizes in smaller size cuts at the expense of impactor resolution. Sample acquisition times for Auger samples were on the order of 30 to 60s in comparison to 30 to 90 min for a normal impactor sample.

6.2 General Experimental Procedure

Although several types of experiments were performed to explore the effects of temperature, coal composition, and stoichiometric ratio on ash formation, all of the experiments followed the same general procedure. At the beginning of each experiment a number of stoichiometry calculations were performed to predict the total combustion air flow and CO₂ concentration necessary for a given coal feedrate and stoichiometric ratio (1.2 was generally the target S.R.). The furnace was then slowly heated with natural gas until the

TABLE 6.1-3. - Compounds used to prepare 1000 ppm AA standard

Element Standard	Compound	Mass for 1ℓ of standard soln
Al	AlCl ₃	2.471
Si	Na ₂ SiF ₆	6.696
Ca	Ca(OH) ₂	1.849
Fe	Fe(NO ₃) ₂ · 9H ₂ O	7.234
Na	NaCl	1.907
K	KCl	2.542
Mg	MgCl ₂ · H ₂ O, Mg(OH) ₂	8.4209, 2.399

exhaust temperature reached 400° to 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 one-half hour, a temperature profile of the furnace was measured (as previously discussed). When the measured gas concentrations were restabilized after the temperature profile measurement (approximately 10 to 15 min), the furnace gas composition was determined and noted 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, the impactor 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 was 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 measurement, was repeated.

6.3 Summary of Experiments

A list summarizing the base case experiments performed is given in Table 6.3-1. The table shows the burn number, coal, approximate feed rate, and measured peak temperature. The raw numbers are listed in Appendix F. Burns 13 through 35 were considered base

TABLE 6.3-1. - Summary of base case experiments

Burn	Coal	Feed Rate (kg/hr)	Peak Temperature (K)
13	Beulah Lignite	2.8	1601
14	Beulah Lignite	2.7	1596
15	Eagle Butte	3.4	1745
16	Eagle Butte	2.7	1684
17	Kentucky No. 9	1.9	1711
18	Kentucky No. 9	1.9	1746
19	Illinois No. 6	2.0	1665
20	Illinois No. 6	1.9	1632
21	Illinois No. 6	1.9	1635
22	Beulah Lignite	2.7	1567
23	Eagle Butte	2.6	1548
24	Kentucky No. 9	1.8	1684
27	Kentucky No. 11	1.7	1593
28	Kentucky No. 11	2.1	1613
30	Loy Yang 2301	2.4	1536
31	Loy Yang 2301	2.3	1477
32	Upper Freeport	1.7	1620
34	Upper Freeport	1.9	1573
35	Upper Freeport	1.9	1573

case burns. Two types of impactor samples were acquired during these burns: full and total filter. Full impactor samples used all the impactor plates and a "total filter" was determined by summing the results of all the plates. The total filter sample used only the pre-separator, plate 1, and the after-filter. Replicate samples and burns were acquired to test reproducibility. In burns 21 through 24, one full impactor sample was acquired for CCSEM analysis.

Temperature profiles in the combustor were those that occurred naturally and were altered by changing coal feed rate. Increasing coal feed rates and keeping the stoichiometric ratio at 1.2 can raise peak temperatures, but it shortens residence times. Burns 36 through 40 modified the temperature profiles by significantly changing coal feed rates.

Residence times at each sampling port varied with test burn conditions. For example, at port 6 residence times (calculated) ranged from 1 to greater than 3s. A list of residence times for each experiment is contained in Appendix E.

Table 6.3-2 lists the summary of burns 36 through 40. Due to good reproducibility in the base case burns, only full impactor samples were obtained. The first sample for AA analysis was taken at conditions closely resembling the base case, and two samples were acquired at a modified feed rate.

Loy Yang is a low ash coal with high ash sodium content. Two burns of Loy Yang 2301 doped with extraneous kaolinite were performed to elucidate sodium interactions with aluminosilicates. Pulverized kaolinite, obtained from Burgess Pigment Company, was very fine and tended to agglomerate. This led to feeding difficulties which were at least partially overcome by placing another pneumatic vibrator on the feed line at the exit of the screw feeder. Enough kaolinite was added to significantly alter the ash content, and also to mimic the sodium to silica ratio found in Beulah Lignite.

Kentucky No. 11 was doped with extraneous sodium acetate trihydrate (NaAc) because it was a high ash low sodium coal, and rich in illite (potassium aluminosilicate). Two burns of doped Kentucky No. 11 were performed to gain information about sodium interactions with aluminosilicates in addition to studying potassium evolution. Enough NaAc was added to raise the sodium to silica ratio to that found in Beulah Lignite. Table 6.3-3 shows the summary of the doped burns.

6.3-2. - Summary of modified temperature profile experiments

Burn	Sample	Coal	Feed Rate (kg/hr)	Peak Temperature (K)
36	A	Kentucky No. 9	1.9	1646
36	B,C	Kentucky No. 9	0.7	1514
37	A	Kentucky No. 11	2.1	1534
37	B,C	Kentucky No. 11	0.5	1378
38	A	Beulah Lignite	2.9	1558
38	B,C	Beulah Lignite	1.3	1405
39	A	Loy Yang 2301	2.4	1533
39	B,C	Loy Yang 2301	3.8	1613
40	A	Eagle Butte	3.4	1633
40	B,C	Eagle Butte	1.2	1508

TABLE 6.3-3. - Summary of doped coal burns

Burn	Sample	Coal	Feed Rate (kg/hr)	Peak Temperature (K)
41	A	Loy Yang 2301 + 94 g Kaolin/kg coal	2.7	1243
42	A	Loy Yang 2301 + 94 g Kaolin/kg coal	2.1	1640
42	B	Loy Yang 2301 + 94 g Kaolin/kg coal	3.5	1611
43	A	Kentucky No. 11 + 99 g NaAc/kg coal	1.8	1559
43	B	Kentucky No. 11 + 99 g NaAc/kg coal	4.0	1733
44	A	Kentucky No. 11 + 99 g NaAc/kg coal	1.8	1531

In burns 42 through 44 impactor samples were cut in half before AA analysis. Half of the sample was dissolved in acid, as in previous samples, for total ash analysis. The other half was dissolved in DI water in an effort to discern between captured (fixed) sodium from that which was condensed.

Burns 47 through 50 were performed in conjunction with a visiting investigator from PSIT who operated an in situ particle probe. In situ particle size, velocity, and concentration measurements were performed with an Insittec Measurement Systems Particle Counting Sizing and Velocimetry device (PCSV-P) (Holve et al. (1979), Holve et al. (1980), Holve (1980)).

Since the outside diameter of the PCSV-P was larger than the combustor sample ports, modifications to the combustor were made near port 14 to allow insertion of the probe. In addition to in situ particle size distributions, full impactor samples were acquired for AA analysis, and abbreviated impactor samples were taken for CCSEM analysis. A summary of burns 46 through 50 is shown in Table 6.3-4. In addition to the samples acquired at combustor port 11, samples were acquired from port 5 in burns 47 and 48. Results from this testing are described in both Section 6 and Section 7 of this report.

The final six experiments, burns 51 through 54 and 59-60, used Phase II beneficiated and blended coals. Burns 51 and 54 used Illinois No. 6 SOAP (Spherical Oil Agglomeration Product). The cleaning processes and fuel analysis for these coals were discussed in Section 3 of this report.

TABLE 6.3-4 - Summary of burns which obtained AA and CCSEM samples, and PCSV particle size distributions

Burn	Sample (port)	Coal	Feed Rate (kg/hr)	Peak Temperature (K)
47	A (11) C (5)	Illinois No. 6	1.3	1577
47	E (11) G (5)	Illinois No. 6	2.4	1633
48	A (11) C (5)	Beulah Lignite	1.6	1433
48	E (11)	Beulah Lignite	2.6	1518
49	A (11)	Loy Yang 2301	1.8	1548
49	G (11)	Loy Yang 2301	2.7	1766
50	E (11)	Loy Yang 1953	2.5	1433

Although some preliminary data were obtained for Illinois No. 6 SOAP, feeding difficulties made the results questionable. Unlike the parent coal, SOAP formed sticky particles at relatively low temperatures which adhered to burner cooling tubes. This problem might be related to the asphalt binder used in processing of the SOAP, as it was not noted in burns of the parent coal. Over the time of the experiment, the collection of sticky coal particles blocked the burner and the experiment was aborted. Only a single sample was acquired for each burn before shutting down.

Burns 52 and 53 used a coal that was cleaned by a molten caustic leach process: Kentucky No. 9 7A. The cleaning process for this coal was also discussed in Section 3. For both the Illinois No. 6 SOAP and Kentucky No. 9 Gravimelt 7A burns, all samples were taken at sample port 11. During Phase II, experiments were also conducted with the Eagle Butte/Kentucky #9 70/30 wt/wt blend discussed in Section 3, and with Phase I Kentucky 9, Kentucky 11, and Eagle Butte to assess iron-aluminosilicate interactions. These experiments are summarized in Table 6.3-5.

TABLE 6.3-5 - Summary of burns with cleaned coals and additional baseline coal burns

Burn	Sample	Coal	Feed Rate (kg/hr)	Peak Temperature (K)
51	A	Illinois #6 SOAP	1.6	1583
52	A	Kentucky #9 Gravimelt 7A	1.9	1690
53	A	Kentucky #9 Gravimelt 7A	1.8	1587
54	A	Illinois #6 SOAP	2.3	1599
56	C	Kentucky #11	1.3	1513
56	F	Kentucky #11	2.1	1702
59	A	Eagle Butte/Kentucky #9 Blend	1.8	1470
60	A	Eagle Butte/Kentucky #9 Blend	1.8	1480
61	A	Eagle Butte	2.1	1466
67	A	Kentucky #9	1.7	1499

6.4 Coal Characterization - UA Supplemental Analysis

Analysis of coals studied in this program was conducted by the University of Kentucky, the University of North Dakota Energy and Environmental Research Center (UNDEERC), and Foster Wheeler Development Co. with the exception of Loy Yang 2301, which was analyzed by the State Electricity Commission of Victoria (SECV), Australia. Detailed analysis of Phase I coal samples was provided in the Phase I Final Report (Boni et al., 1990). A summary of the Phase I coal data and analysis of Phase II coals was provided in Sections 3 (ultimate, proximate, CCSEM summaries) and 4 (detailed CCSEM and other advanced analytical technique results) of this report.

The original and doped burns of Loy Yang 2301 (burns 30, 31, 39, 41, and 42) used a coal that was received crushed, not pulverized. A typical length scale of the crushed Loy Yang 2301 was 1000 μm (1 mm) and larger. The other six coals in the base suite (all Phase I coals except San Miguel, which could not be burned successfully at UA) were received pulverized such that 70% was smaller than 200 mesh (74 μm). The crushed Loy Yang 2301 size scale was reduced by using a household blender. The product from the blender was screened (hole size 1 x 1 mm) and the large fraction returned to the blender. Only the fraction passing through the screen was allowed in the feeder bin. It should be noted that during screening and pulverization of the crushed Loy Yang 2301, relatively large shards of broken glass were found. The clear pieces of glass that were found were removed,

but remaining glass may have affected the combustion ash. AA analysis showed the glass to be high in silica. Burn 49 used another sample of Loy Yang 2301 which was received pulverized. Analysis was assumed to be the same as that of the crushed material.

A calculated ash analysis for the doped coals (Loy Yang 2301 with kaolinite, and Kentucky No. 11 with sodium acetate) is included in this section.

6.4.1 Loy Yang 2301 Supplemental Analysis

A separate analysis was provided with each barrel of the Loy Yang 2301 examined at UA. These data are presented in Table 6.4-1.

6.4.2 Gravimelt 7A Moisture Analysis

Kentucky No. 9 7A had a high moisture content and required drying. This coal arrived enclosed in a plastic bag inside a 55 gallon drum that was lined with a plastic sleeve. On the inside sleeve and inside of the plastic bag was a significant amount of condensed moisture. Due to this large amount of water and tendency for the coal to adhere to itself, it was laid out to dry in open air before burning. A moisture analysis was performed on the as-received and dried coals.

The moisture analysis was conducted by placing a known mass of sample in an oven at approximately 110°C. The mass of the sample was determined as a function of time. Results for the coal as-received, dried coal used in burn 52, and dried coal used in burn 53 are shown in Figure 6.4-1. The as-received coal was measured to be approximately 50% moisture compared to the reported values (Table 3.7, Section 3) of 17 to 47%. The dried coals had approximately 15 and 20% moisture for burns 52 and 53 respectively.

FIGURE 6.4-1. - Moisture analysis of UA Gravimelt 7A.

TABLE 6.4-1. Loy Yang 2301 fuel analysis

Dry Basis, Barrel:	1	2	3	4
Proximate Analysis				
Fixed carbon	47.1	46.7	47.1	46.8
Volatile matter	51.0	51.4	51.0	51.2
Ash	1.9	1.9	1.9	2.0
Moisture	15.6	13.3	13.4	13.0
Ultimate Analysis				
Carbon	67.0	67.1	67.2	67.1
Hydrogen	4.9	4.9	4.9	4.9
Oxygen (diff)	25.37	25.29	25.19	25.16
Nitrogen	0.53	0.52	0.51	0.55
Sulfur	0.30	0.29	0.30	0.29
Ash	1.9	1.9	1.9	2.0
Moisture	15.6	13.3	13.4	13.0
H.H.V., MJ/kg	26.2	26.1	26.2	26.1
Coal Inorganics (% DB)				
Al	0.03	0.02	0.02	0.02
Fe (NP)	0.08	0.06	0.06	0.06
Ca	0.05	0.06	0.04	0.04
Mg	0.19	0.19	0.19	0.19
Na	0.53	0.49	0.51	0.51
Cl	0.75	0.76	0.76	0.75
Coal Minerals (% DB)				
SiO ₂	0.18	0.20	0.15	0.21
Al ₂ O ₃	<0.1	<0.1	<0.1	<0.1
K ₂ O	<0.1	<0.1	<0.1	<0.1
TiO ₂	0.01	0.01	0.01	0.01
FeS ₂	0.0	0.0	0.0	0.0
Total (% DB)				
S	0.30	0.29	0.30	0.29
Fe	0.08	0.06	0.06	0.06
Al ₂ O ₃	0.060	0.060	0.040	0.04

6.4.3 Analysis of Doped Coal Samples

Loy Yang was a low ash coal whose ash had a high sodium content. Loy Yang 2301 was doped with extraneous kaolinite to study sodium interactions with aluminosilicates. Table 6.4-2 shows the calculated ash chemistry of Loy Yang 2301 doped with 94g of kaolinite per kg additive-free coal. Calculations were performed using an average chemical analysis of kaolinite supplied by Burgess Pigment Company (BP). Comparison of kaolinite compositions provided by BP and a chemical analysis by atomic absorption is shown in Table 6.4-3.

Kentucky No. 11 was doped with extraneous sodium acetate trihydrate because it was a high ash coal, low in sodium, and high in illite (a potassium containing aluminosilicate). Experiments with doped Kentucky No. 11 were performed to gain information about sodium interactions with aluminosilicates in addition to studying potassium evolution. Table 6.4-4 shows the calculated ash chemistry of Kentucky No. 11 doped with 99g sodium acetate trihydrate per kg additive-free coal.

TABLE 6.4-2. Calculated ash analysis for doped and undoped Loy Yang 2301

Loy Yang 2301	Undoped	Undoped	Doped	Doped
Oxides	% AR*	Fraction Oxide	% AR*	Fraction Oxide
Al ₂ O ₃	0.04	0.036	3.36	0.404
SiO ₂	0.16	0.132	4.02	0.483
CaO	0.06	0.047	0.05	0.006
Fe ₂ O ₃	0.08	0.066	0.07	0.009
Na ₂ O	0.60	0.490	0.55	0.066
K ₂ O	< 0.01	0.004	< 0.01	0.001
MgO	0.28	0.225	0.25	0.030
Total	1.9		10.21	
*AR denotes as-received.				

TABLE 6.4-3. - Kaolinite analysis

Oxides	BP Analysis	AA Analysis	
	wt %	wt %	± error
Al ₂ O ₃	37.5-39.7	31.38	0.46
SiO ₂	44.8-45.3	42.95	0.70
CaO	N/A	0.000	0.0047
Fe ₂ O ₃	trace	0.899	0.024
Na ₂ O	N/A	0.0665	0.0026
K ₂ O	N/A	0.2182	0.0035
MgO	N/A	0.0717	0.0028
TiO ₂	1.35-2.27	N/A	N/A

TABLE 6.4-4. - Calculated ash analysis for doped (with sodium acetate trihydrate) and undoped Kentucky No. 11

Kentucky No. 11	Undoped	Undoped	Doped	Doped
Oxides	% AR*	Fraction Oxide	% AR*	Fraction Oxide
Al ₂ O ₃	4.99	0.246	4.54	0.224
SiO ₂	10.27	0.506	9.34	0.460
CaO	0.45	0.022	0.41	0.020
Fe ₂ O ₃	2.74	0.135	2.45	0.012
Na ₂ O	0.06	0.003	1.58	0.078
K ₂ O	0.63	0.031	0.57	0.028
MgO	0.28	0.014	0.26	0.013
Total	20.29		2.030	

*AR denotes as-received.

6.5 Experimental Results

A summary of experiments was presented in Subsection 6.3. In this section, detailed results of the experimental effort which involved burning the coals at a stoichiometric ratio of 1.2 are presented. Data presented in this chapter are organized into groups related to experimental goals: base case burns, modified feed rate/temperature profile burns, doped coal experiments, burns with in situ particle distribution measurement, and burns of cleaned coals. Listings of raw data are found in Appendix F.

Results presented in this chapter include the measured temperature profiles for each experiment. Since heating in the combustor was supplied by the burning fuel alone, the temperature profiles were those that occurred naturally at the combustion conditions of the experiment. Measured temperatures were also expected to be lower than the actual gas temperature due to radiation losses by the thermocouple to the combustor walls.

Atomic absorbance (AA) analysis results of size-segregated fly ash impactor samples were presented in two ways: fraction oxide plots, and ash concentration plots. For the fraction oxide plots, the mass of each of the seven measured elements as oxides were presented as a fraction of the total mass measured on a stage in a stacked bar chart. This allowed immediate inspection of relative enrichments or depletions of specific elements.

For each fraction oxide plot, the ash analysis normalized to seven elements measured (Al, Si, Ca, Fe, Na, K, and Mg) was presented as the first bar from the left. The next bar to the right was the total filter analysis. The total filter was calculated as the sum of mass from all the impactor stages. Impactor stage one was just to the right of the total filter bar and gave the ash composition of the largest particles measured. The smallest size class (after-filter) was the furthest bar on the right in the fraction oxide plot. The intermediate bars were the results of analysis from the size classes smaller than plate 1 and larger than the after-filter with size decreasing from left to right. Since graphics allowed only six oxides to be plotted, the seventh, magnesium was the difference between the top of the bar and one. Each bar was labeled with the impactor stage number and sample letter.

Ash concentration plots showed the relative mass of ash in each size class presented as the log of the calculated ash concentration versus impactor stage. The ash concentration was calculated from the measured concentration in dissolving acid of each of the seven elements as oxides as determined from AA analysis. Assuming an AA solution density of one, the total mass sampled could be determined. Using a known sampling dilution rate, the measured furnace NO_x concentration, and the measured diluted sample NO_x concentration the volume of sampled flue gas could be calculated. Knowing the total sampled mass and total sampled flue volume, an ash concentration was calculated in mg per standard cubic meter.

The ash concentration was also calculated from the coal feed rate and flue gas flow rate assuming complete combustion. Both coal feed rate and flue gas flow rate were determined from known input air flow rates and stoichiometry. This concentration was the

first bar on the left of the ash concentration plots and was typically higher than the total ash concentration determined by impactor sampling. This was attributed primarily to loss to the walls of the combustor in the form of slag. Inspection of the combustor walls and the ash trap after a burn showed significant amounts of slag.

In the following subsections, there are some reported instances in which calculated ash flows do not agree with measured ash flows. This was attributed to ash retention in the furnace. In several experiments, fairly large quantities of slag were collected in the ash trap. In addition, ash retention of at least the more volatile elements was discovered in the furnace during the first set of CCSEM/Mössbauer sampling runs (approximately burns 32 - 35). Subsequent to this, the furnace was heated with natural gas to an exhaust temperature of 500°C (peak temperature of approximately 1500°C) and held at the temperature for approximately 8 hr before changing coals. This served to remove any residual ash and to "smooth" any slag that may have been protruding into the central portion of the furnace.

6.5.1 Base Case Burns - Phase I Coals

The base case burns were performed to examine trends in mineral matter transformations for the base suite of coals. In addition to providing preliminary data on inorganic matter interactions, results from these experiments also directed later experiments which investigating specific mechanisms.

Another goal of the base case burns was to test the fly ash sampling system. For this reason, replicates of total filter samples and full impactor samples were acquired (Subsection 6.3). To check reproducibility, plots for the base case burns show all the data for the fraction oxide plots. For clarity however, only the average is presented in the ash concentration plots.

6.5.1.1 Burns 13 and 14 Beulah Lignite

Figures 6.5-1 and 6.5-2 show temperature profiles for burns 13 and 14 respectively. Both had feed rates of approximately 2.5 kg/hr. The two measured temperature profiles as a function of axial distance were in good agreement.

Fraction oxide plots for burns 13 and 14 are shown in Figures 6.5-3 and 6.5-4 respectively, and the ash concentration plots are shown in Figures 6.5-5 and 6.5-6. There was some discrepancy between the total filter ash compositions and those of the parent coal ash. The ash analysis showed a higher fraction of aluminum, calcium, and a lower fraction for sodium. The reasons for these difference were not clear.

Trends shown by the two fraction oxide plots were in general agreement, with the most distinct feature being the enrichment of sodium in the smaller size classes. A slight enrichment of potassium in the small sizes was also noted.

FIGURE 6.5-1. - Temperature profile for burn 13, Beulah.

FIGURE 6.5-2. - Temperature profile for burn 14, Beulah.

Run 13 Beulah Lignite

FIGURE 6.5-3. - Fraction oxide plot for burn 13.

Run 14 Beulah Lignite

FIGURE 6.5-4. - Fraction oxide plot for burn 14.

FIGURE 6.5-5. - Ash concentration for burn 13.

FIGURE 6.5-6. - Ash concentration for burn 14.

In addition to plate 1 (the largest size class) silicon and aluminum showed a slight maximum in the middle size classes around 2 to 3 μm . This could be due to silicate particles originally present in the parent coal which were only slightly changed during the combustion process. The size distributions of kaolinite and mixed silicate matter in the parent coal (Section 3) showed a large fraction of these particles in the $<2.5 \mu\text{m}$ size class. A $1.5 \mu\text{m}$ particle of density 2.63 g/cm^3 would have an aerodynamic diameter (diameter measured by the impactor) of $2.0 \mu\text{m}$ (Hinds (1982)). This suggests that the mode of silicates in the 2 to 3 μm range might be due to clay particles present in the parent coal that did not coalesce or only slightly coalesced during combustion.

Ash concentration plots for burns 13 and 14 were in general agreement. The total filter analysis was lower than the calculated ash flow in the combustor by a factor of approximately five. This was attributed to significant slagging and fouling of combustor walls. Approximately 1% of the measured mass was found in the after-filter.

6.5.1.2 Burns 15 and 16 Eagle Butte

Results for burns with eagle butte are shown in Figures 6.5-7 through 6.5-12. The temperature profiles are shown in Figures 6.5-7 and 6.5-8 for burns 15 and 16 respectively. The fraction oxide plots are shown in Figures 6.5-9 and 6.5-10, and the ash concentration plots are shown in Figures 6.5-11 and 6.5-12.

The temperature profile for burn 15, with a coal feed rate of 3.4 kg/hr , peaked a little sooner and approximately 60 K higher than for burn 16 with a feed rate of 2.7 kg/hr . The temperature profiles were otherwise similar. There was again some discrepancy between the ash analysis and the total filter analysis. Fractions of aluminum and calcium were again higher in the ash analysis than for the total filter for reasons which were not clear.

Both burns 15 and 16 showed a slight enrichment of sodium in the smallest size classes. Burn 15 suggested a slight enrichment of potassium in the small size classes but burn 16, with the higher temperatures, did not show enrichment of potassium in the small sizes.

The largest size class showed an enrichment of silicon, most likely due to large quartz particles found in the parent coal. Aluminosilicates, as represented by the aluminum fraction, appeared to be evenly distributed over all but the largest size classes. The aluminum behavior was also consistent with the parent coal mineralogy.

Calcium was notably enriched in the smaller sizes. This could be due to calcite present in the parent coal (3 wt% of mineral matter). Calcium in the middle size classes might have been a result of calcium rich miscellaneous mixed minerals present in the parent coal shown in Table 3.IX (15 wt% of mineral matter).

Ash concentration plots (Figures 6.5-11 and 6.5-12) again showed good agreement. The total filter was lower than the calculated ash concentration by a factor of approximately four. This was attributed to fouling and slagging of combustor walls. Mass on the after-filter accounted for less than 1% of the measured ash mass.

FIGURE 6-5.7. - Temperature profile for burn 15, Eagle Butte.

FIGURE 6.5-8. - Temperature profile for burn 16, Eagle Butte.

Run 15 Eagle Butte

FIGURE 6.5-9. - Fraction oxide plot for burn 15.

Run 16 Eagle Butte

FIGURE 6.5-10. - Fraction oxide plot for burn 16.

FIGURE 6.5-11. - Ash concentration for burn 15.

FIGURE 6.5-12. - Ash concentration for burn 16.

6.5.1.3 Burns 17 and 18 Kentucky No. 9

Results of burns of the bituminous coal Kentucky No. 9 are shown in Figures 6.5-13 through 6.5-18. Temperature profiles for burns 17 and 18 (both with a feed rate of 1.9 kg/hr) are shown in Figures 6.5-13 and 6.5-14 respectively and show good agreement. Fraction oxide plots are shown in Figures 6.5-15 and 6.5-16, and ash concentration plots are shown in Figures 6.5-17 and 6.5-18.

The total filter analysis showed good agreement between burns and also with the ash analysis. There was some discrepancy between fraction oxide plots in the middle to smaller size classes for the two burns. The principal dissimilarity was exhibited in the silicon behavior: burn 18 showed a higher silicon fraction in smaller size classes than burn 17.

A slight enrichment of sodium was noted for burn 18 and especially for burn 17. Potassium was evenly distributed throughout the impactor which is consistent with potassium existing primarily in the mineral illite, and low sodium and low chlorine for this coal. Alkali bound by the mineral matter was expected to be less likely to vaporize, especially in the absence of displacement or extraction mechanisms attributable to vapor phase sodium and chlorine. This is discussed further in Chapter 5.

Calcium was also enriched in the small sizes for both burns 17 and 18. This was likely due to calcite present (3 wt% of mineral matter) and relative deficiency of other calcium rich minerals in the parent coal.

The ash concentrations showed comparable results. Again the measured ash mass was less than the calculated ash concentration based on coal and air feed rates. Less than 1% of the measured mass was found on the after-filter, suggesting little vaporization of inorganic species for this coal.

6.5.1.4 Burns 19 and 20 Illinois No. 6

Results obtained using the Illinois No. 6 coal are shown in Figures 6.5-19 through 6.5-24. The temperature profile for burn 19, with a feed rate of 2.0 kg/hr, is shown in Figure 6.5-19, and Figure 6.5-20 shows burn 20 with a feed rate of 1.9 kg/hr. The temperature profiles show good agreement with burn 19 being slightly higher.

Fraction oxide plots are shown in Figures 6.5-21 and 6.5-22 for burns 19 and 20 respectively. The total filter analysis agrees well with the ash analysis. The ash analysis is, however, slightly higher in calcium and slightly lower in potassium.

The fraction of aluminum was fairly constant over all size classes with a slight depletion in the smallest sizes. This might be due to a slight enrichment of silicon and calcium in the smallest size class.

FIGURE 6.5-13. - Temperature profile for burn 17, Kentucky #9.

FIGURE 6-5.14. - Temperature profile for burn 18, Kentucky #9.

Run 17 Kentucky No. 9

FIGURE 6.5-15. - Fraction oxide plot for burn 17.

Run 18 Kentucky No. 9

FIGURE 6.5-16. - Fraction oxide plot for burn 18.

FIGURE 6.5-17. Ash concentration for burn 17.

FIGURE 6.5-18. - Ash concentration for burn 18.

FIGURE 6.5-19. - Temperature profile for burn 19, Illinois #6.

FIGURE 6.5-20. - Temperature profile for burn 20, Illinois #6.

Run 19 Illinois No. 6

FIGURE 6.5-21. - Fraction oxide plot for burn 19.

Fraction Oxide vs Impactor Stage

FIGURE 6.5-22. - Fraction oxide plot for burn 20.

FIGURE 6.5-23. - Ash concentration for burn 19.

FIGURE 6.5-24. - Ash concentration for burn 20.

The small size classes showed a slight enrichment of sodium for burn 19 but not for burn 20. The potassium fraction appeared to be almost constant for all size classes. As with the Kentucky No. 9 burns, this was consistent with the potassium bound in the mineral matter (illite and miscellaneous silicate). It could be speculated that the low sodium in this coal reduced the effects of displacement, and the low chlorine content lessened the effects due to an extraction mechanism that might allow potassium to escape the mineral matter in which it was contained.

Calcium was slightly enriched in the small size classes for both burn 19 and burn 20. This could be due to calcite which dominated the form of the calcium in the parent coal.

The ash concentration plots shown in Figures 6.5-23 and 6.5-24 agree fairly well, with the total filter again showing less mass (approximately 56%) than that calculated from the coal feed rate. Less than one half of a percent of the measured mass was found on the after-filter.

6.5.1.5 Burn 27 and 28 Kentucky No. 11

Figures 6.5-25 through 6.5-30 show results obtained for Kentucky No. 11. The temperature profiles shown in Figures 6.5-25 and 6.5-26 agreed well for feed rates of 1.8 and 2.1 kg/hr for burns 27 and 28 respectively.

The total filter samples agreed well with the ash analysis as shown in the fraction oxide plots in Figures 6.5-27 and 6.5-28. As with the Illinois No. 6 results, the ash analysis was slightly higher for calcium, but slightly lower for potassium than the total filter analysis.

The fraction of aluminum was fairly constant over all size classes whereas silicon was depleted in the smallest size class. This was consistent with the parent coal mineralogy which showed a large fraction of the aluminum-containing species (kaolinite, illite, and mixed silicates) in the small size classes, and quartz shifted to the middle size classes. Although the sodium content of Kentucky No. 11 was very low, there was a slight enrichment of this alkali in the small size classes. Potassium however, behaved much like the potassium in the Kentucky No. 9 and Illinois No. 6 coals: the fraction of potassium was relatively constant throughout all the size classes. This was consistent with the aluminum behavior, since mineral bound potassium would be expected to follow the potassium-containing aluminosilicate species (illite and mixed silicates).

Calcium was again enriched in the small size classes, and again calcite was the dominant calcium-containing mineral in the parent coal. A small fraction of gypsum was also present.

Ash concentration plots (Figures 6.5-29 and 6.5-30) were in fairly good agreement. Again the measured ash concentration was smaller than the calculated ash concentration. The measured concentration was lower by a factor of approximately two and a half. The approximate mass on the after-filter accounted for merely 0.1% of the measured mass.

FIGURE 6.5-25. - Temperature profile for burn 27, Kentucky #11.

FIGURE 6-5.26. - Temperature profile for burn 28, Kentucky #11.

Run 27 Kentucky No. 11

FIGURE 6.5-27. - Fraction oxide plot for burn 27.

Run 28 Kentucky No. 11

FIGURE 6.5-28. - Fraction oxide plot for burn 28.

FIGURE 6.5-29. Ash concentration for burn 27.

FIGURE 6.5-30. - Ash concentration for burn 28.

6.5.1.6 Burn 29 Natural Gas (blank)

Figures 6.5-31 and 6.5-32 show the results of a background check in a "worst-case" scenario. To clean out the combustor, one or two burns with natural gas were conducted between burns which used different coals. Generally, the number and duration of natural gas burns depended on the extent of fouling and slagging observed for each coal used in previous burns. The combustor was further cleaned during heat-up which used natural gas.

Sampling for burn 29 was conducted for the first natural gas burn subsequent to using San Miguel (a high ash coal) in burn 25. Both burn 24 and 25 which used San Miguel coal fouled and plugged the fire tube resulting in a shut down. The plug was broken up and removed with the aid of a long rod leaving a significant quantity of material on the walls. Several cleaning burns were required to remove the wall material. Burn 29 was the first such cleaning burn after burn 25. Sampling was also performed shortly after the combustor reached temperatures which were typically sufficient for self-sustained pulverized coal combustion which ensured that the combustor was not significantly cleaned. Under these sampling conditions, the background was expected to be a "worst-case".

The fraction oxide plot shown in Figure 6.5-31 shows a background which was high in aluminum, silicon, and iron. Magnesium, calcium, potassium and sodium were relatively depleted. The smaller size classes were dominated by silica for reasons which were not clear.

Typical cascade impactor sample times for a coal burn were on the order of 30 min. During this burn, the impactor collection occurred over a period in excess of 3 hr. Extended sample times allowed for collection of a greater sample volume of flue gas. Figure 6.5-32 showed that measured concentrations of ash in the flue gas were one to two orders of magnitude lower than concentrations during a typical coal burn. This "worst-case" experiment suggested that contamination from coal to coal during experimental burns was not a significant contribution to the sampled fly ash mass.

6.5.1.7 Burns 30 and 31 Loy Yang 2301

Loy Yang was an interesting coal because of its low ash content and high sodium fraction in the ash. Unfortunately, this coal also had small shards (~ 1 mm) of glass contaminant. This was reflected in the results for this coal which are presented in Figures 6.5-33 through 6.5-38.

Temperature profiles for burns 30 (2.4 kg/hr) and 31 (2.3 kg/hr) are shown in Figures 6.5-33 and 6.5-44 respectively. The profiles paralleled each other with the peak temperature for burn 30 approximately 60 K higher than for burn 31.

Run 29 Natural Gas (Blank)

FIGURE 6.5-31. - Fraction oxide plot for burn 29, natural gas.

FIGURE 6.5-32. Ash concentration for burn 29.

FIGURE 6.5-33. - Temperature profile for burn 30, Loy Yang 2301.

FIGURE 6.5-34. - Temperature profile for burn 31, Loy Yang 2301.

Although this coal was pulverized, as discussed in Subsection 6.4 some large coal particles remained and were observed during fly ash sampling during burn 30. A number of particles were observed glowing as the fly ash sample traversed the translucent polypropylene sample line. Exhaust temperatures were also unusually high, 950 K compared to 670 to 770 K for previous burns of other coals. This may have been due to the observation of coal burning in the ash trap. This observation was confirmed 12 hr after the burn was completed when glowing embers were discovered in the ash trap.

To avoid the excessive burnout times, the coal for burn 31 was pulverized more extensively. The coal feeder was emptied and all the coal was pulverized using a blender before it was loaded into the feeder. Although this did not completely solve the problem, it did appear to contribute to a significant reduction in burnout times.

The total filter samples shown in the fraction oxide plots of Figures 6.5-35 and 6.5-36 showed a large variation and did not agree with the ash analysis. In general, the total filter samples showed a much higher fraction of silicon than the ash analysis. The fraction of silicon in each size class was also highly variable. Observations of average trends did suggest a substantial enrichment of sodium in the small size classes. Determining trends from the fraction oxide plots was difficult primarily due to the silicon behavior. This erratic behavior was blamed on extraneous glass that was discovered in the raw coal. This conclusion was supported by AA analysis of the glass which showed it to be high in silicon.

Run 30 Loy Yang

FIGURE 6.5-35. - Fraction oxide plot for burn 30.

Run 31 Loy Yang

FIGURE 6.5-36. - Fraction oxide plot for burn 31.

FIGURE 6.5-37. Ash concentration for burn 30.

FIGURE 6.5-38. - Ash concentration for burn 31.

It was believed that the extraneous glass was also responsible for the measured ash concentration to be higher than the concentration based on the coal feed rate for burn 30. Measured and calculated ash concentrations for burn 31 were identical. Based on previous results from other coals, this result was also unexpected.

6.5.1.8 Burns 34 and 35 Upper Freeport

Results from burns of Upper Freeport are shown in Figures 6.5-39 through 6.5-44. Feed rates of approximately 1.9 kg/hr in both burns 34 and 35 resulted in temperature profiles (Figures 6.5-39 and 6.5-40) which agreed well.

The fraction oxide plots shown in Figures 6.5-41 and 6.5-42 demonstrated good reproducibility and also agreed well with the ash analysis. A minor difference was that the fraction of calcium and magnesium in the ash analysis was slightly higher than the total filter samples.

One of the most notable features of the fraction oxide plots was enrichment of silicon in the submicron size range. This behavior was seemingly contradictory to the parent coal mineralogy. Quartz was concentrated in the 5 to 40 μm range and the concentration of aluminosilicates in the <2.5 μm size class was higher than that for the quartz.

Only a very slight enrichment of sodium in the small sizes was noted for burns 34 and 35. The potassium fraction was almost a constant with perhaps a slight depletion in the smallest size classes. Calcium showed a small enrichment in the smaller sizes and was almost depleted in the largest size class.

The total measured mass of fly ash was again less than that calculated from the coal feed rate (approximately 33%). The mass of ash on the after-filter was approximately 0.1% of the total.

6.5.2 Modified Feed Rate/Temperature Profile Burns - Phase I Coals

A series of burns was conducted in an effort to elucidate the effect of temperature on fly ash elemental partitioning. In each of these burns an impactor sample was acquired at conditions which were as similar as possible to the original base case burn for that coal. Reproducing the temperature profiles of the base case burns proved difficult since slagging and deterioration required rebuilding the upper portion of the combustor prior to these experiments. Extension of a refractory support at approximately sample port 4 in effect provided cooling that did not exist in the previous construction.

After acquisition of the first impactor sample at base conditions, the coal feed rate was changed in an attempt to change the overall temperature profile. Input air flows were altered appropriately to keep the stoichiometric ratio at 1.2. Changing the fuel rate altered the total heat output which in turn modified the temperature profile. In some cases, a minor

FIGURE 6.5-39. - Temperature profile for burn 34, Upper Freeport.

FIGURE 6-5.40. - Temperature profile for burn 35, Upper Freeport.

Run 34 Upper Freeport

FIGURE 6.5-41. - Fraction oxide plot for burn 34.

Run 35 Upper Freeport

FIGURE 6.5-42. - Fraction oxide plot for burn 35.

FIGURE 6.5-43. Ash concentration for burn 34.

FIGURE 6.5-44. - Ash concentration for burn 35.

temperature change was instituted by preheating the primary input air. Two impactor samples were collected at the new conditions.

Coals burned in these experiments were Kentucky No. 9, Kentucky No. 11, Beulah Lignite, Loy Yang 2301, and Eagle Butte. Results presented for the modified feed rate experiments were similar to those presented in the previous section for the base case burns. Two uncorrected temperature profiles were presented for the high and low temperature experiments plotted on the same figure. Two fraction oxide plots and two ash concentration plots were presented: one each for the base burn and one each that was an average of the two samples collected at the modified conditions.

6.5.2.1 Burn 36 Kentucky No. 9

Results from burn 36 are shown in Figures 6.5-45 through 6.5-49. Temperature profiles are presented in Figure 6.5-45. The higher feed rate (1.9 kg/hr) had a higher peak temperature of 1650 K which was approximately 140 K higher than 1510 K for the lower feed rate (0.7 kg/hr). The profile for the higher feed rate peaked higher and sooner than that for the lower feed rate which was most likely due to a shorter burnout time at the higher temperatures.

The fraction oxide total filters showed excellent agreement between the two different temperature burns, and good agreement with the ash analysis. As with the base burn, the ash analysis showed a slightly greater fraction of calcium than did the total filter analysis.

The low temperature burn showed enrichment of calcium and iron in the small sizes with the exception of the after-filter. Enrichment of iron in the small sizes for the high temperature burn was not evident and calcium enrichment was visible only for impactor plate 8.

Aluminum behavior did not change significantly for the two burns, but silicon behavior did. The higher temperature burn showed a silicon enrichment in the smaller sizes with respect to the lower temperature burn. This was conceivably due to vaporization of silicon through the sub-oxide.

Sodium showed a slight enrichment in the small sizes for the low temperature burn but not for the high temperature burn. Enrichment of the small sizes in potassium was more evident than sodium for both temperatures. However, potassium enrichment in the small size classes was more conspicuous for the low temperature burn.

The total filter ash concentration was lower than that calculated from the coal feed rate for both feed rates. The total filter ash concentration, however was slightly lower for the higher feed rate suggesting a greater loss to the walls. In both cases nearly 90% of the measured mass was on the top impactor stage.

FIGURE 6.5-45. - Temperature profiles for burn

FIGURE 6.5-46. - Fraction oxides for burn 36

FIGURE 6.5-47. - Fraction oxides for burn 36 low temperature.

FIGURE 6.5-48. - Ash concentration for burn 36 high temperature.

FIGURE 6.5-49. - Ash concentration for burn 36 low temperature.

The ash concentration showed noticeably different profiles for the two temperatures. More mass was in the smaller sizes for the high temperature burn which possibly suggested char fragmentation at the higher temperature.

6.5.2.2 Burn 37 Kentucky No. 11

The temperature profiles for burn 37 are shown in Figure 6.5-50. The fraction oxide plots are shown in Figures 6.5-51 and 6.5-52, and the ash concentration plots are shown in Figures 6.5-53 and 6.5-54. The two feed rates were 2.1 kg/hr for the high feed rate, and 0.5 kg/hr for the low feed rate. The difference between measured peak temperatures was approximately 155 K. The peak for the higher feed rate was approximately 1535 K and for the lower it was approximately 1380 K.

The fraction oxide plots for burn 37 are shown in Figures 6.5-51 and 6.5-52. The total filter analysis for the two feed rates showed excellent agreement. Comparison of the total filter analysis and the ash analysis showed good agreement. Both fraction oxide plots exhibited enrichment of silicon in the small size classes and a relative depletion of aluminum.

Iron was depleted in the smallest sizes classes for both coal feed rates, but the depletion was more marked for the lower temperature burns. Calcium was enriched in the smaller sizes with the exception of the after-filter for both burns. Potassium and the small sodium fraction appears primarily in the middle size classes with a relative depletion in the smallest size cuts.

FIGURE 6.5-50. - Temperature profiles for burn 37, Kentucky #11.

FIGURE 6.5-51. - Fraction oxides for burn 37 high temperature.

FIGURE 6.5-52. - Fraction oxides for burn 37 low temperature.

FIGURE 6.5-53. - Ash concentration for burn 37 high temperature.

FIGURE 6.5-54. - Ash concentration for burn 37 low temperature.

The total filter ash concentrations agreed well between the two feed rates for burn 37. The ash concentration profiles showed a slight movement of mass from stages two through four in the low temperature burn, to stages five through the after-filter in the high temperature burn. This could have been due to greater char fragmentation at higher temperatures.

6.5.2.3 Burn 38 Beulah Lignite

Figure 6.5-55 shows the two temperature profiles for burn 38. The higher feed rate (2.9 kg/hr) resulted in a measured peak temperature of 1558 K, and the peak temperature for the lower feed rate (1.3 kg/hr) was approximately 1405 K. The result was an approximate 150 K difference.

The total filter sample of the fraction oxide plots, (Figures 6.5-56 and 6.5-57) showed good agreement not only between the high and low temperature burns but also with the base case burns (burns 13 and 14). The most prominent feature of both the high and low temperature fraction oxide plots was enrichment of sodium in the smaller sizes suggesting vaporization. Sodium enrichment of the small sizes was much more marked for the low temperature burn which suggested that reaction of sodium with silicates, which would reduce the amount of sodium in the vapor, was more important at the higher temperature.

FIGURE 6.5-55. - Temperature profiles for burn 38, Beulah.

FIGURE 6.5-56. - Fraction oxides for burn 38 high temperature.

Run 38 Beulah Lignite Lo T

FIGURE 6.5-57. - Fraction oxides for burn 38 low temperature.

The measured total filter samples of the ash concentration plots (Figures 6.5-58 and 6.5-59) agreed well between the two feed rates, but were significantly lower than the calculated ash concentration. The profiles showed movement of mass from stages two through four in the low temperature burn to stages five through seven in the high temperature burn. No change in mass was noted for stages eight and the after-filter at the two temperatures.

6.5.2.4 Burn 39 Loy Yang 2301

As was mentioned in Subsection 4.1, pieces of glass were discovered in this coal. Prior to burn 39, great care was taken to remove all visible glass shards. This proved difficult and tedious, but resulted in smooth fraction oxide and ash concentration profiles. The uncorrected temperature measurements for burn 39 (Figure 6.5-60) showed strikingly similar profiles. The peak temperature for the higher feed (3.8 kg/hr) rate was approximately 1615 K, and for the lower feed rate (2.4 kg/hr) it was 1535 K yielding an approximate 80 K difference.

Fraction oxide plots (Figures 6.5-61 and 6.5-62) showed some variation between the two burns, with a greater fraction of silicon shown for the lower temperature sample. Other than differences in silicon results, significant differences were not notable between fraction oxide plots.

FIGURE 6.5-58. - Ash concentration for burn 38 high temperature.

FIGURE 6.5-59. - Ash concentration for burn 38 low temperature.

FIGURE 6.5-60. - Temperature profiles for burn 39, Loy Yang 2301.

FIGURE 6.5-61. - Fraction oxides for burn 39 high temperature.

FIGURE 6.5-62. - Fraction oxides for burn 39 low temperature.

Most of the silicon and iron was in larger sizes for both high and low feed rates. Sodium enrichment of small sizes was very marked. Although the potassium fraction of the ash analysis was very small, potassium in the total filter was significant. Potassium was also enriched in the smaller sizes. Magnesium was a large fraction of the ash analysis, but had a smaller fraction in the total filter analysis. The magnesium fraction showed a maximum at plate six for both burns.

The ash concentration (Figures 6.5-63 and 6.5-64) for the total filter sample was lower than that calculated for the ash analysis for both burns, and the total filter for the high temperature burn was lower than that for the low temperature burn. The ash concentration profiles for Loy Yang 2301 showed distinct differences from other coals examined in this study. Loy Yang 2301 fly ash had a significant fraction of the sampled mass in the small size classes. This could be attributed to a relatively high concentration of vaporized alkali. The high sodium to silica ratio for the parent coal suggested that capture of sodium by silicates would be less important for this coal.

6.5.2.5 Burn 40 Eagle Butte

Temperature profiles for burn 40, which burned Eagle Butte, are presented in Figure 6.5-65. The feed rate for the higher temperature burn was approximately 3.4 kg/hr which resulted in a peak temperature of approximately 1633 K. The lower feed rate was approximately 1.2 kg/hr yielding a measured peak temperature of 1508 K, which was approximately 125 K lower.

FIGURE 6.5-63. - Ash concentration for burn 39 high temperature.

FIGURE 6.5-64. - Ash concentration for burn 39 low temperature.

FIGURE 6.5-65. - Temperature profiles for burn 40, Eagle Butte.

The total filter samples of the fraction oxide plots (Figures 6.5-66 and 6.5-67 again agreed well for the two burns, with a slight depletion of silicon in the high temperature burn with respect to the low temperature burn. Silicon was depleted in the small particles for the high temperature burn, whereas aluminum was slightly depleted in the smallest size classes for the low temperature burn.

Calcium and magnesium were enriched in the small sizes for the high temperature burn. Potassium and sodium were enriched in the small sizes for both burns, and was more conspicuous for the low temperature burn.

The ash concentration for the low temperature burn total filter sample was higher than for the high temperature burn sample (Figures 6.5-68 and 6.5-69). The ash concentration profile for the lower temperature burn was relatively flat for stages two through the after-filter, with a slight decrease in the smallest sizes. A slight maximum in the ash concentration profile was noted for the low temperature burn at stage six. This maximum was more marked for the high temperature burn. A minimum at stage three was also noted for the high temperature burn. There appeared to be a relative movement of mass from the larger sizes to the smaller sizes for the high temperature burn when compared to the low temperature burn results.

6.5.3 Doped Coal Experiments - Phase I Coals

Burns 41 through 44 used two parent coals which were doped with additive. Burns 41 and 42 used Loy Yang 2301 doped with kaolinite to study sodium reaction with inherent

FIGURE 6.5-66. - Fraction oxides for burn 40 high temperature.

FIGURE 6.5-67. - Fraction oxides for burn 40 low temperature.

FIGURE 6.5-68. - Ash concentration for burn 40 high temperature.

FIGURE 6.5-69. - Ash concentration for burn 40 low temperature.

versus extraneous silicates. To study the influence of sodium on potassium behavior, burns 43 and 44 used Kentucky No. 11 doped with sodium acetate.

Loy Yang was chosen to study sodium-silicate interactions because of its relatively high sodium to silicate ratio, and low silicates. Kentucky No. 11 was chosen to study effects of sodium on potassium behavior because of the relatively high illite content of the parent coal. Illite, a potassium aluminosilicate, in Kentucky No. 11 also exhibited a size distribution shifted to relatively small sizes (Sections 3 and 4).

6.5.3.1 Burns 41 and 42 Loy Yang 2301 Doped with Kaolinite

Additive for burns 41 and 42 was 94g of kaolinite (Burgess Pigment Company) per kg additive-free-pulverized-Loy Yang 2301. The quantity of additive was sufficient to significantly alter the mineralogy and also mimic the sodium-to-silicon ratio in Beulah Lignite. Kaolinite particles were estimated at greater than approximately $0.65\ \mu\text{m}$ in size as evidenced by impactor samples acquired during burns 41 and 42. Kaolinite had the consistency of flour and was mixed with the pulverized coal to exist in an extraneous manner.

Known amounts of pulverized Loy Yang and kaolinite were mixed by hand in three steps. The first step involved scooping small amounts of coal into a plastic bag with the entire amount of kaolinite. The blend was stirred until homogeneous to the eye. This procedure was continued until approximately one-third of the coal was combined with additive. The second step involved scooping small amounts of kaolinite-coal blend into a barrel containing the remaining two-thirds of unadulterated coal. When approximately half the mixture had been combined in the barrel, the other half was placed in the barrel and mixed with a paddle. The entire barrel mixture was shaken then stirred with the paddle several times. Thirdly, the mixture was screened, mixed, laid out on a plastic sheet to dry for 16 hr, and finally placed in the feeder.

Feeding the fuel proved difficult due to bridging in the screw feeder. Unfortunately only one impactor sample was acquired in burn 41 before coal stopped feeding due to catastrophic bridging. The bridging problem was at least partially overcome in burn 42 by connecting a vigorous vibrator to the screw feeder. Two different feed rates and corresponding impactor samples were obtained for burn 42.

Temperature profiles for burns 41 and 42 are shown in Figures 6.5-70 and 6.5-71 respectively. Burn 41 had a relatively low peak temperature of approximately 1243 K and an approximate feed rate of 2.7 kg/hr. The lower feed rate for burn 42 was approximately 2.1 kg/hr and the higher was 3.5 kg/hr. Peak temperatures were approximately 1640 K and 1611 K respectively. Although the lower feed rate had a higher measured peak temperature, the higher feed rate had a higher average temperature. This was not observed in the parent coal during burn 39 (Subsection 6.5.2.4). Apparently, addition of dopant affected more than just silicate content, however an explanation was not immediately obvious.

FIGURE 6.5-70. - Temperature profiles for burn 41, LY 2301 + kaolinite.

FIGURE 6.5-71. - Temperature profiles for burn 42, LY 2301 + kaolinite.

Fraction oxide plots for burns 41 and 42 are shown in Figures 6.5-72 through 6.5-74. Figure 6.5-72 for burn 41, which had the lowest peak temperature, showed the greatest enrichment of sodium on the after-filter. This was consistent with burn 38 Beulah Lignite results (Subsection 6.5.2.3) suggesting capture of sodium by silicates through reaction. It was interesting to note that the kaolinite showed an almost bimodal mass size distribution with a maximum at stage 1 and another at approximately stages 5 and 6 with a drop in the submicron range.

Comparison of results from burn 39, which used undoped Loy Yang 2301 (Subsection 6.5.2.4), to results from burns 41 and 42 showed a significant change in sodium distribution. Addition of silicate to the coal could have affected sodium through two separate mechanisms. The first is enhanced capture through reaction due to an increase in concentration of silicates. The second mechanism affecting the sodium distribution is condensation. Additional silicate matter could contribute added condensation sites for vaporized sodium. To determine the relative fraction of capture versus condensation, impactor samples from burn 42 were split into two portions. One portion was subjected to normal dissolution using dissolving acid, as with all previous samples. The second portion was placed in an equivalent quantity of deionized (DI) water. The former was representative of total sodium present, and the latter the condensed fraction.

FIGURE 6.5-72. - Fraction oxides for burn 41.

FIGURE 6.5-73. - Fraction oxides for burn 42 low feed.

FIGURE 6.5-74. - Fraction oxides for burn 42 high feed.

The preseparator cup was split into two nearly equal portions of known mass. Difference in mass could then be compensated for in later analysis. Impaction substrate filters were cut into two pieces of nearly equal size. The sample on each piece was approximately half the original mass with an error of approximately $\pm 5\%$ for stages 1 and 2, and less than 5% for subsequent stages. Larger error in plates 1 and 2 was the result of large sample loadings in that size class. Larger samples were prone to spillage and loss.

Fraction oxide plots for water soluble samples were dominated by alkali, although other species were present in minor quantities. Presentation of these plots would not be instructive since it was nearly all alkali. Further discussion of results is left to Subsection 6.6.

6.5.3.2 Burns 43 and 44 Kentucky No. 11 Doped with Sodium Acetate

Burns 43 and 44 used identical coal blends: Kentucky No. 11 doped with 98.86g sodium acetate trihydrate (NaAc) per kg additive-free coal. The additive significantly raised the sodium content and also mimicked the sodium-to-silicon ratio in Beulah Lignite. Choice of Kentucky No. 11 was due to its high illite content and low occurrence of sodium. NaAc was added to the parent coal to exist in an extraneous manner.

NaAc granules were broken up by hand and screened into the coal. The mixture was blended until homogeneous to the eye then screened a second time to break up any undetected agglomerates. NaAc particles were in general larger than the coal particles which ensured that the sodium would be initially external to char particles during combustion.

Burn 43 proved to be somewhat difficult. Some of the difficulties included evidence of a leak in the fire tube, malfunctioning temperature probe, a leak in the particle sampling system, and a unique plug in the combustor exhaust. Due to these difficulties, a replication of burn 43 was attempted in burn 44.

Two full impactor samples were acquired in burn 43 corresponding to the two temperature profiles shown in Figure 6.5-75. Figure 6.5-76 shows the temperature profile for burn 44. The first impactor sample for burn 43, sample A, corresponded to an approximate feed rate of 1.8 kg/hr and approximate peak temperature of 1559 K. For burn 43 sample B, the peak temperature was approximately 1733 K with a feed rate of roughly 4.0 kg/hr. Burn 44 had an approximate feed rate of 1.8 kg/hr and peak temperature of 1531 K. The fraction oxide plot for burn 43 sample A, with lower peak temperature, is shown in Figure 6.5-77. Sample B, with higher peak temperature, fraction oxide plot is shown in Figure 6.5-78, and Figure 6.5-79 is for burn 44.

The total filter for both samples collected in burn 43 showed good agreement with the calculated ash analysis, while the total filter for burn 44 was lower in overall sodium content. As expected, all three samples showed a higher fraction of sodium on all stages compared to the parent coal (Subsections 6.5.1.3 and 6.5.2.2).

FIGURE 6.5-75. - Temperature profiles for burn 43, Ky #11 + NaAc.

FIGURE 6.5-76. - Temperature profile for burn 44, Ky #11 + NaAc.

FIGURE 6.5-77. - Fraction oxides for burn 43 sample A.

FIGURE 6.5-78. - Fraction oxides for burn 43 sample B.

FIGURE 6.5-79. - Fraction oxides for burn 44.

All three fraction oxide plots from burns 43 and 44 also showed a greater fraction of potassium in the small sizes, although this observation was less marked burn 44. Sodium enrichment of the smaller sizes was also evident, especially for burn 44, however the after-filter was dominated by silicon. This could have been due to a large fraction of small quartz particles in this coal (Sections 3 and 4). A more thorough discussion of burns 43 and 44 can be found in Subsection 6.6.2.

6.5.4 UA/PSIT Test Burns with In Situ Particle Distribution Measurement

Size distributions of fly-ash samples extracted from a combustor may be affected by the extraction process itself. For example, the high quench rate in a sample extraction probe can cause existing vapor species to condense homogeneously and heterogeneously. Other factors, including coagulation of fly ash particles in sample lines, can influence resulting measured size distribution. It would be desirable to compare fly ash size distributions measured by extraction and collection via cascade impactor, with in situ optical size distribution measurements. Measurements of size distributions with the two techniques could yield information on distribution biasing due to extractive sampling. Burns 47 through 50 acquired extracted samples and also made in situ fly ash size distribution measurements. Results of these measurements are presented in this section.

Ash particle size distributions were measured during a series of burns conducted in the down-fired combustor at the University of Arizona. During burns of four coals, ash samples were acquired using the cascade impactor sample system discussed previously, and ash size distributions were measured using an in situ particle counting sizing and velocimetry

instrument (PCSV-P) (Holve and Self (1979, 1980), Holve (1980)). Samples were collected with the cascade impactor for analysis by atomic absorbance (AA) as in previous experiments, and samples were sent to the University of Kentucky for computer controlled scanning electron microscopy (CCSEM) analysis. Impactor samples analyzed by AA, inversions of cascade impactor data (Appendix D), and PCSV-P distributions are presented and discussed in this section.

Modifications to the down-fired combustor were required to allow utilization of the PCSV-P. Sample port 14 was removed and a four inch diameter hole was cut into the fire tube (nominal port size was 2 in.) such that the top of the PCSV-P was approximately 5.05m down from the burner. Refractory was cast and mated to the fire tube for mechanical support of the PCSV-P. Refractory plugs were also cast to seal the four inch port when not in use by the PCSV-P and also to seal the fire tube when the refractory supports were removed.

CCSEM and Mössbauer analysis require relatively large sample mass in comparison to AA analysis. However, typical impactor samples have a large percentage of the collected mass on the top impactor plate (stage 1). In some cases 90% of the mass may be found on the top plate. To increase sample mass in smaller size cuts for CCSEM analysis, several of the lower impactor plates were combined and sample acquisition times were increased. Cascade impactor samples acquired for CCSEM analysis consisted of three size segregated samples: plate 1, plates 2 through 4, and plates 5 through the after-filter. Visual inspection of samples suggested that particle bounce and reentrainment may have occurred with the extended sample times due to an inordinate amount of mass on the top stage. Particle bounce in the impactor would tend to shift mass distributions to smaller sizes.

Each of the four coals burned in this set of experiments focussed on mechanisms important in different particle size ranges. Previous results suggested large fly ash particle interactions could be studied with burns of Illinois No. 6. Beulah Lignite showed interesting behavior in all size ranges and Loy Yang was of interest due to significant production of small fly ash particles. Table 6.5-1 summarizes experiments and samples acquired during each burn. Impactor samples for AA and CCSEM analysis were acquired from combustor sample port 11 as in all previous burns (Subsections 6.5.1 through 6.5.3). Samples were also collected from port 5 in burns 47 and 48.

Ideally an in situ probe would not affect combustion conditions. However, it should be noted that the relative size of the PCSV-P compared to the inside diameter of the fire tube could significantly affect flow in the combustor. Inserting the isokinetic sample probe into the combustor reduced the flow area to approximately 90% of the original whereas the PCSV-P reduced the flow area to approximately 37% of the original. Also, radiation losses to the relatively large water cooled jacket surrounding the PCSV-P (4-in. outside diameter compared to the 6-in. inside diameter of the fire tube) could change the temperature profile observed by the evolving fly-ash size distribution.

TABLE 6.5-1. - Summary of experiments and acquired samples

Burn No.	Coal	Feed Rate (kg/hr)	Samples
47	Illinois No. 6	1.3	AA*, CCSEM*, PCSV-P
47	Illinois No. 6	2.4	AA*, CCSEM*
48	Beulah Lignite	1.6	AA*, CCSEM*, PCSV-P
48	Beulah Lignite	2.8	AA, CCSEM, PCSV-P
49	Loy Yang 2301	1.8	AA, CCSEM, PCSV-P
49	Loy Yang 2301	2.7	AA, CCSEM, PCSV-P
50	Loy Yang 1953	2.5	AA, CCSEM, PCSV-P
*Sample acquired from port 5 as well as port 11.			

6.5.4.1 Burn 47 Illinois No. 6

Burn 47 used Illinois No. 6 coal at two different feed rates (approximately 1.3 and 2.4 kg/hr). Cascade impactor samples were acquired for AA and CCSEM analysis from ports 11 and 5 for both feed rates. PCSV-P distributions were measured for the lower feed rate only. Figure 4.80 shows the uncorrected temperature profiles for the two feed rates.

6.5.4.1.1 Impactor Results

6.5.4.1.1.1 Sample Port 11

Figure 6.5-80 shows AA results as fraction oxide of the ash versus cascade impactor stage for the lower feed rate. The ash fraction oxide plot for the higher feed rate, and higher temperature, is shown in Figure 6.5-81.

The total filter of the fraction oxide plots agreed well with the ash analysis. Figures 6.5-81 and 6.5-82 were also consistent with results presented previously for Illinois No. 6 (Subsection 6.5.1.4). The plot for the lower feed rate, and lower peak temperature, showed a slight sodium enrichment in the smaller size ranges suggesting vaporization. Sodium enrichment in the small sizes was not as evident for the higher feed rate, and higher peak temperature, which was consistent with previously reported results for Beulah Lignite suggesting capture of sodium by chemical reaction with silicate matter (Boni, et al., (1990), Gallagher, et al., (1990)).

FIGURE 6.5-80. - Temperature profiles for burn 47, Illinois #6.

FIGURE 6.5-81. - Fraction oxide for 1.3 kg/hr feed rate.

FIGURE 6.5-82. - Fraction oxide for 2.4 kg/hr feed rate.

Figures 6.5-83 and 6.5-84 show the concentration of ash in mg/sm^3 for the cascade impactor samples. For both cases the ash concentration was lower than that calculated from the ash analysis of the coal (approximately 50%) and were consistent with concentrations reported for burns 19 and 20 (Subsection 6.5.1.4). Errors in measurements of concentrations were dominated by determination of sample volumes for the larger size cuts and was estimated at less than approximately $\pm 5\%$. For smaller size cuts errors in measurements of silicon and aluminum also contributed due to lower concentrations and difficulty in measurement. Errors were estimated at less than $\pm 12\%$ for the smaller size ranges. Although the effect of temperature on ash concentration was slight, it does appear that a small shift of mass to smaller sizes was noted for the higher coal feed rate relative to the lower feed rate.

6.5.4.1.1.2 Sample Port 5

Figure 6.5-85 showed the fraction oxide plot for the impactor sample acquired from port 5 at the lower feed rate, and Figure 6.5-86 was for the higher feed rate. Comparison of Figures 6.5-85 and 6.5-86 to Figures 6.5-81 and 6.5-82 showed more enrichment of sodium and potassium in smaller sizes for samples acquired from port 5. This was likely due to a higher concentration of unreacted and uncondensed alkali species existing in the vapor during sampling at port 5 relative to port 11. Condensation and nucleation of vapor species most likely occurred in the sample probe at port 5.

FIGURE 6.5-83. - Ash concentration for 1.3 kg/hr feed rate.

FIGURE 6.5-84. - Ash concentration for 2.4 kg/hr feed rate.

Run 47 Illinois No 6 C

FIGURE 6.5-85. - Fraction oxide for 1.3 kg/hr feed rate.

Run 47 Illinois No 6 G

FIGURE 6.5-86. - Fraction oxide for 2.4 kg/hr feed rate.

For samples acquired in both ports 11 and 5 enrichment of alkali in the small sizes was more pronounced for the lower coal feed rate, and lower temperature, than for the higher coal feed rate. This might suggest that a significant fraction of alkali capture (due to chemical reaction with silicate matter) occurred before port 5. Figure 6.5-87 however, showed the fraction of the sampled alkali that appeared in the small sizes (impactor plate 8 plus the after-filter) was higher in the port 5 samples for the higher feed rate. This was most likely due to a shorter residence time. After port 5 the subsequent reduction of the fraction of alkali in the small sizes was greater for the higher feed rate, and higher temperature. Capture of alkali due to reaction with silicate matter was the most likely explanation for the reduction of alkali in the small sizes since condensation would be less likely at the higher temperatures observed at the higher feed rate.

Although the mass of alkali in the small sizes was greater for the higher feed rate, the fraction oxide showed that a greater fraction of the mass in the small sizes for the lower feed rate was due to alkali. Greater relative enrichment of sodium in the small sizes for both low temperature (low feed rate) samples compared to high temperature samples could be explained by a shift of non-alkali mass to small sizes for high temperature burns. The slight shift of mass to small sizes was shown for samples acquired in both ports 5 and 11. Ash

FIGURE 6.5-87. - Fraction of alkali in the small sizes for the high feed rate (HI) and the low feed rate (LO) from port 5 and 11 samples.

concentration plots for port 5 samples are shown in Figures 6.5-88 and 6.5-89, and for port 11 samples in Figures 4.83 and 4.84 for 1.3 and 2.4 kg/hr feed rates respectively. Inspection of oxide cumulative fraction plots (not shown here) and fraction oxide plots suggest that calcium might be a least partially to blame for greater mass in the small sizes for the high temperature burn, but aluminum was not.

6.5.4.1.2 PCSV-P Results

Figure 6.5-90 shows the normalized cumulative and density mass distributions for samples acquired with the PCSV-P during the Illinois No. 6 burn. Since the range varied from sample to sample, the mean was determined only over an overlapping range. Distributions were normalized over the abbreviated range and averaged together. The averaging technique allowed for presentation of only one distribution when making comparisons, but shortened the range and slightly shifted cumulative distributions to larger sizes. In addition, PCSV-P distributions were not weighted to account for different sample measurement times. For these reasons, a plot of all PCSV-P mass distributions with respective means are presented. Figure 6.5-91 shows the mean of the area distribution and Figure 6.5-92 shows the mean of the number distribution for burn 47.

FIGURE 6.5-88. - Ash concentration for 1.3 kg/hr feed rate.

FIGURE 6.5-89. - Ash concentration for 2.4 kg/hr feed rate.

FIGURE 6.5-90. - Mass distributions for burn 47.

FIGURE 6.5-91. - Area distribution for burn 47.

FIGURE 6.5-92. - Number distributions for burn 47.

A comparison of the PCSV-P mean mass distribution, mass as determined from AA analysis of impactor samples, and the impactor inversion is shown in Figures 6.5-93 and 6.5-94. PCSV-P mass distributions were determined from the number distributions by assuming a particle density of one. The PCSV-P counted char particles as well as ash particles. AA analysis did not measure carbon content and thus did not measure actual particle distributions but inorganic matter size distributions using aerodynamic diameters. If there was a significant amount of unburned char in the ash, the two measurements could differ. It would be expected, however, that unburned char would be relatively large ($> 9 \mu\text{m}$) and would be collected on the top two stages of the impactor. In addition, the PCSV-P did not measure the finest particles which were collected on the after-filter of the cascade impactor. The smallest sizes typically reported with the PCSV-P were $0.4 \mu\text{m}$ and the impactor after-filter was a $0.2 \mu\text{m}$ flouropore filter. If there was a significant number of small particles, results from the PCSV-P would report a size distribution shifted to larger sizes when compared to AA results. Results from Figures 4.93 and 4.94 showed fairly good agreement considering the impactor cutoff diameter for the top stage was $9 \mu\text{m}$. However, approximately 90% of the sampled mass in the impactor was on the top stage.

Additional analysis of PCSV-P data is provided in Section 7 of this report.

FIGURE 6.5-93. - Impactor and PCSV-P psd for burn 47.

FIGURE 6.5-94. - Impactor and PCSV-P for burn 47.

6.5.4.2 Burn 48 Beulah Lignite

Burn 48 used Beulah Lignite coal at two different feed rates of approximately 1.65 and 2.8 kg/hr. Cascade impactor samples were acquired for AA and CCSEM analysis from port 11 for both feed rates, and at port 5 for the lower feed rate. PCSV-P distributions were measured for both feed rates. Figure 6.5-95 shows the uncorrected temperature profiles.

6.5.4.2.1 Impactor Results

6.5.4.2.1.1 Sample Port 11

Figure 6.5-96 shows AA results as a fraction oxide versus cascade impactor stage plot for the lower feed rate. Figure 6.5-97 is for the higher feed. The total filter of the fraction oxide plots differed from the ash analysis, however Figures 6.5-96 and 6.5-97 were consistent with results presented previously for Beulah Lignite in burns 13, 14 and 38 (Subsections 6.5.1.1 and 6.5.2.3). The silicon fraction however, was slightly higher in burn 48. Plots for both feed rates showed sodium enrichment in the smaller size ranges suggesting vaporization. Sodium enrichment in the small sizes was not as marked for the higher feed rate, and higher peak temperature. These results were consistent with previous burns of Beulah Lignite which suggested capture of sodium due to reaction with silicate matter. Faster reaction and capture would occur at higher temperatures resulting in less sodium in the vapor available for condensation or nucleation in the small size classes.

FIGURE 6.5-95. - Temperature profiles for burn 48, Beulah.

FIGURE 6.5-96. - Fraction oxide for 1.65 kg/hr feed rate.

FIGURE 6.5-97. - Fraction oxide for 2.8 kg/hr feed rate.

Figures 6.5-98 and 6.5-99 show the concentration of ash in mg/sm^3 for the impactor samples. As with burn 47, the ash concentration was lower than that calculated from the ash analysis of the coal, but was consistent with concentrations reported for burns 13, 14, and 38. Concentration measurement errors for larger size cuts were estimated at less than $\pm 5\%$, and less than $\pm 6\%$ for smaller size cuts. The mass of sample on plate 8 and the after-filter was less for the high temperature burn. Inspection of the sodium distribution, which is not presented, suggested that less mass in the small sizes for the high temperature burn was likely due to capture of sodium by particles in the larger size classes.

6.5.4.2.1.2 Sample Port 5

The fraction oxide plot for the impactor sample acquired at the lower feed rate is shown in Figure 6.5-100. The ash concentration plot is shown in Figure 6.5-101. Figure 6.5-100 showed a significant enrichment of sodium in the small sizes. Comparison of Figures 6.5-98 and 6.5-101 showed more mass on the after-filter for the sample acquired at port 5. Attributing a cause for a higher observed mass on the after-filter for the port 5 sample with respect to the port 11 sample proved difficult possibly due to competing effects. Inspection of elemental distribution plots, which were not included here, suggest that the sodium may not have completely vaporized when the sample was acquired at port 5: the fraction of sampled sodium in the small sizes was higher for the port 11 sample. Vaporization of sodium would move more sodium to smaller measured sizes when sampling

FIGURE 6.5-98. - Ash concentration for 1.65 kg/hr feed rate.

FIGURE 6.5-99. - Ash concentration for 2.8 kg/hr feed rate.

FIGURE 6.5-100. - Fraction oxide for burn 48 port 5.

FIGURE 6.5-101. - Ash concentration for burn 48 port 5.

at port 11 relative to port 5. Capture of sodium, however appears to have increased the mass of sodium in the 1 to 2 μm sized particles. A greater fraction of sampled silicon also appeared on plate 8 and the after-filter for the port 5 sample. Although the mass of silicon in the small sizes was slight, it did appear that coagulation or agglomeration of small silicon containing particles may have moved silicon mass to larger sizes for the port 11 sample.

6.5.4.2.2 PCSV-P Results

Figures 6.5-102 and 6.5-103 show the normalized PCSV-P measured cumulative mass and mass density distributions for low and high feed rates of Beulah Lignite respectively. Mean distributions are also presented. Comparison of mean mass distributions is shown in Figure 6.5-104 for the two feed rates. Figure 6.5-105 shows the mean of area distributions and Figure 6.5-106 shows the mean number distributions. Distributions at the higher feed rate appeared to have more mass in the 2 to 10 μm range and less in the 0.4 to 2 μm than at the lower feed rate. This was consistent with AA impactor results from samples obtained at port 11 shown in Figure 6.5-107.

FIGURE 6.5-102. - Mass distribution for burn 48 low feed rate.

FIGURE 6.5-103. - Mass distribution for burn 48 high feed rate.

FIGURE 6.5-104. - Mass distributions for burn 48.

FIGURE 6.5-105. - Area distributions for burn 48.

FIGURE 6.5-106. - Number distributions for burn 48.

FIGURE 6.5-107. - Cumulative mass versus cutoff diameter for burn 48.

Comparison of PCSV-P mean mass distributions, mass as determined from AA analysis of impactor samples, and impactor inversion are shown in Figures 6.5-108 through 6.5-111 for both feed rates. Although the distributions were in general agreement, comparison of impactor data to PCSV-P distributions showed a shift to smaller sizes for the impactor results. Also, the impactor inversion showed a more marked increased mass in the middle sizes for higher feed rate than the PCSV-P distributions. Both measurement techniques do show modes less than $10\ \mu\text{m}$ for the low feed rate shown in Figure 6.5-108. The impactor distribution in Figure 6.5-110 at the higher feed rate would seem to suggest that there were modes less than $10\ \mu\text{m}$, whereas the PCSV-P distribution showed a tail in the same size range.

6.5.4.3 Burn 49 Loy Yang 2301

Burn 49 used pulverized Loy Yang 2301 at two different feed rates of approximately 1.8 and 2.7 kg/hr. This coal arrived already pulverized. Previous burns used crushed coal pulverized in the laboratory. Prior to pulverizing, extraneous shards of glass were found and removed. It was assumed as-received pulverized coal did not have extraneous glass. Burn 49 impactor samples were acquired for AA and CCSEM analysis from port 11, and PCSV-P distributions were measured for both feed rates. Figure 6.5-112 shows uncorrected temperature profiles for the two feed rates.

FIGURE 6.5-108. - Impactor and PCSV-P psd for burn 48, differential.

FIGURE 6.5-109. - Impactor and PCSV-P psd for burn 48, simulative.

FIGURE 6.5-110. - Impactor and PCSV-P psd for burn 48, differential, high feed rate.

FIGURE 6.5-111. - Impactor and PCSV-P psd for burn 48, cumulative, high feed rate.

FIGURE 6.5-112. - Temperature profile for burn 49, Loy Yang 2301.

6.5.4.3.1 Impactor Results

Figure 6.5-113 shows AA results as fraction oxide versus cascade impactor stage for the lower feed rate. Figure 6.5-114 is for the higher feed. As with previous burns of Loy Yang 2301, sodium was highly enriched in the small sizes. Contrary to previous burns of Loy Yang 2301 however, burn 49 samples differed significantly for the two feed rates. Differences in silicon behavior was most noted: 98% of sampled Si was on stage 1 for sample acquired at the lower feed rate whereas only 40% was found on plate 1 for the higher feed rate. Differences in calcium behavior were also significant: of sampled Ca, 75% was on stage 1 for the lower feed rate and 50% was on stage 1 for the higher feed rate. Magnesium also showed differences with 50% and 30% of sampled Mg found on stage 1 for low and high feed rates respectively.

Comparison to burn 39 (Subsection 6.5.2.4), showed that Figure 6.5-114 was more representative of previous burns of Loy Yang 2301 than Figure 6.5-113. Mg and Ca fractions were, however higher in Figure 6.5-114 than in burn 39. Differences could have been related to undetected extraneous impurities, but this was difficult to discern.

Figures 6.5-115 and 6.5-116 show ash concentration (mg/sm^3) for impactor samples. As expected from behavior of Si, Ca, and Mg, mass of sample on stage 1 relative to the rest of the impactor was higher for the lower feed rate.

Run 49 Loy Yang 2301 A

Fraction Oxide vs Impactor Stage

FIGURE 6.5-113. - Fraction oxide for 1.8 kg/hr feed rate.

Run 49 Loy Yang 2301 G

Fraction Oxide vs Impactor Stage

FIGURE 6.5-114. - Fraction oxide for 2.8 kg/hr feed rate.

FIGURE 6.5-115. - Ash concentration for 1.8 kg/hr feed rate.

FIGURE 6.5-116. - Ash concentration for 2.8 kg/hr feed rate.

6.5.4.3.2 PCSV-P Results

Figures 6.5-117 and 6.5-118 show the normalized cumulative mass and mass density distributions acquired with the PCSV-P during low and high feed rates of Loy Yang 2301 respectively. Mean distributions were also presented. Comparison of mean mass distributions are shown in Figure 6.5-119 for the two feed rates. Figure 6.5-120 and 6.5-121 show the mean of the area and number distributions respectively.

Comparison of PCSV-P mean mass distributions, mass as determined from AA analysis, and impactor inversion are shown in Figures 6.5-122 through 6.5-125 for both feed rates. Comparison of impactor data to PCSV-P distributions showed a significant shift to smaller sizes for the impactor results. One possible explanation considered was the relative insensitivity of the PCSV-P in the submicron range compared to the impactor. Since the lower cutoff size for the PCSV-P was approximately $0.4\text{ }\mu\text{m}$, impactor inversions were performed for the impactor data at the low feed rate with the mass response of the lower two stages set to zero. This, in effect, removed mass from the impactor in sizes less than $0.43\text{ }\mu\text{m}$. Comparison to the PCSV-P data is shown in Figures 6.5-126 and 6.5-127. Although the disparity between the two size measuring techniques was smaller, comparisons still differed markedly.

FIGURE 6.5-117. - Mass distribution for burn 49 low feed rate.

FIGURE 6.5-118. - Mass distribution for burn 49 high feed rate.

FIGURE 6.5-119. - Mass distributions for burn 49.

FIGURE 6.5-120. - Area distributions for burn 49.

FIGURE 6.5-121. - Number distributions for burn 49.

FIGURE 6.5-122. - Impactor and PCSV-P psd for burn 49, differential.

FIGURE 6.5-123. - Impactor and PCSV-P psd for burn 49, cumulative.

FIGURE 6.5-124. - Impactor and PCSV-P psd for burn 49, differential, high feed rate.

FIGURE 6.5-125. - Impactor and PCSV-P psd for burn 49, cumulative, high feed rate.

FIGURE 6.5-126. - Imp without 8+AF and PCSV-P psd for burn 49, differential.

FIGURE 6.5-127. - Imp. without 8+AF and PCSV-P psd for burn 49, cumulative.

6.5.4.4 Burn 50 Loy Yang 1953

Burn 50 used Loy Yang 1953 coal at one feed rate of approximately 2.5 kg/hr. Impactor samples were acquired for AA and CCSEM analysis from port 11, and PCSV-P distributions were also measured. Figure 6.5-128 shows the uncorrected temperature profile for burn 50.

6.5.4.4.1 Impactor Results

Figure 6.5-129 shows AA results as fraction oxide versus cascade impactor stage for burn 50. Similar to burn 49 Loy Yang 2301, Figure 6.5-129 showed a significant sodium enrichment in the small size classes for the Loy Yang 1953. Figure 6.5-130 shows ash concentration (mg/sm^3) for the impactor sample. Concentration measurement errors for the larger size cuts was estimated at less than approximately $\pm 5\%$, and less than $\pm 6\%$ for the smaller size cuts. The total filter concentration of ash from the Loy Yang 1953 was similar to that for the Loy Yang 2301, however some differences did exist.

FIGURE 6.5-128. - Temperature profile for burn 50, Loy Yang 1953.

Run 50 Loy Yang 1953 E

Fraction Oxide vs Impactor Stage

FIGURE 6.5-129. - Fraction oxide for 2.5 kg/hr feed rate.

Run 50 Loy Yang 1953 E

Ash Concentration vs Impactor Stage

FIGURE 6.5-130. - Ash concentration for 2.5 kg/hr feed rate.

Comparison of sodium cumulative fraction plots for Loy Yang 2301 (burn 49 Subsection 6.5.4.3) and Loy Yang 1953 (burn 50) is shown in Figure 6.5-131. Although a significant fraction of measured Na for Loy Yang 1953 was found in the smallest sizes, Loy Yang 2301 showed a greater fraction. The ratio of Na to Si was higher for Loy Yang 2301, and greater fraction of Na in the small sizes was consistent with previous results.

6.5.4.4.2 PCSV-P Results

Figure 6.5-132 shows normalized cumulative mass and mass density distributions acquired with the PCSV-P for the burn 50 Loy Yang 1953. Mean distributions are also presented. Figure 6.5-133 and 6.5-134 show the mean area and mean number distributions respectively. Although not as marked as burn 49 Loy Yang 2301, comparison of impactor data to PCSV-P distributions (Figures 6.5-135 and 6.5-136) showed a shift to smaller sizes for the impactor results. It appeared that comparisons of PCSV-P and impactor results showed fairly good agreement for samples with a large fraction of sample in large particle size ranges (9 to 10 μm). However, results diverged as the fraction of mass in the small particle sizes ($< 5 \mu\text{m}$) increased.

FIGURE 6.5-131. - Sodium cumulative fraction for burn 49 and 50.

FIGURE 6.5-132. - Mass distribution for burn 50.

FIGURE 6.5-133. - Area distribution for burn 50.

FIGURE 6.5-134. - Number distribution for burn 50.

FIGURE 6.5-135. - Impactor and PCSV-P psd burn 50, differential.

FIGURE 6.5-136. - Impactor and PCSV-P psd for burn 50, cumulative.

6.5.5 Burns of Cleaned Coals

Comparisons between similar coals which differ mainly in mineral matter contents and compositions would focus on mineral matter transformations rather than coal matrix effects. Ideally, removing mineral matter from a coal and making comparisons between cleaned coal and parent coal would provide just such an opportunity. Although the cleaning process may, and likely does, change the coal matrix to some extent comparisons of cleaned and parent coals can provide some insights to mineral matter transformation during combustion.

Burns 51 through 54 used two coals that were cleaned prior to combustion: Illinois No. 6 SOAP and 7A Kentucky No. 9. Results are presented below for four burns of cleaned coals and Table 6.5-2 summarizes the experiments.

TABLE 6.5-2. - Summary of experiments with cleaned coals

Burn No.	Coal	Feed Rate (kg/hr)
51	Illinois No. 6 SOAP	1.8
52	7A Kentucky No. 9	1.9
53	7A Kentucky No. 9	1.8
54	Illinois No. 6 SOAP	2.3

6.5.5.1 Burns 51 and 54 Illinois No. 6 SOAP

Burns of Illinois No. 6 SOAP (burns 51 and 54) proved difficult due to feeding related problems. This is in contrast to burns of Illinois No. 6 parent coal which showed good feeding characteristics (e.g., burn 47 Subsection 6.5.4.1). Barrels of SOAP emitted strong organic solvent odors when opened suggesting loss of solvent from coal during shipment and storage.

During burns of the SOAP, analysis of gas samples showed extremely unsteady O_2 and CO_2 chart recorder traces and periodic spiking in the CO trace. Visual inspection of the coal flame showed severe pulsing. In a five second span, observations of combustion might include a short period of typically observed combustion followed by a brief period of very active burning and relatively long periods of almost no combustion evident at all. It was difficult to ascertain if this was due to coal self-adhesion in the screw feeder or accumulation of unstable piles of feeding coal above the burner plenum. After the burn, inspection of the burner showed extensive fouling of cooling tubes due to adhesion of sticky coal particles. This was likely due to the asphalt binder in the SOAP.

Temperatures above the plenum were atypically high and coal appeared to ignite quickly upon entering the combustor. This is evidenced in temperature profiles in Figures 6.5-137 and 6.5-138 for burns 51 and 54 respectively. Changing coal feed rate from approximately 1.8 kg/hr in burn 51 to 2.3 kg/hr in burn 54 did not significantly change the temperature profile.

Fraction oxide plots for burns 51 and 54 were shown in Figures 6.5-139 and 6.5-140. Both plots showed good agreement between the total filter sample and the ash analysis. This was also noted for the parent coal in burn 47 discussed in Subsection 6.5.4.1. Burn 51 at the lower feed rate suggested a slight enrichment of Na and Si in the small sizes compared to burn 54 at the higher feed rate. Sample acquired at the higher feed rate showed more Fe in the smaller sizes than the sample acquired at the lower feed rate. It was interesting to note that the composition in each size class was similar. This was also true of the parent coal.

Ash concentration plots are shown in Figures 6.5-141 and 6.5-142. Although the ash concentration measured for the lower feed rate was lower than for the higher feed rate, the sampled mass distributions were very similar. Measured concentration for the SOAP was almost an order of magnitude lower than that measured in burn 47 of Subsection 6.5.4.1 for the parent coal.

FIGURE 6.5-137. - Temperature profile for burn 51, Illinois #6 SOAP.

FIGURE 6.5-138. - Temperature profile for burn 54, Illinois #6 SOAP.

FIGURE 6.5-139. - Fraction oxide for burn 51.

FIGURE 6.5-140. - Fraction oxide for burn 54.

FIGURE 6.5-141. - Ash concentration for burn 51.

FIGURE 6.5-142. - Ash concentration for burn 54.

6.5.5.2 Burns 52 and 53: 7A Kentucky No. 9

Both 7A Kentucky No. 9 and the parent Kentucky No. 9 (during previous burns) showed good feeding and combustion characteristics. The cleaned version (7A), however had a high moisture content and required drying. This coal arrived enclosed in a plastic bag inside a 55 gallon drum lined with a plastic sleeve. On the inside sleeve and plastic bag was a significant amount of condensed moisture. Due to the moisture water and the tendency for self-adhesion, it was laid out to dry in the open air before burning. A moisture analysis was performed on the as-received and dried coals (Subsection 6.4).

Temperature profiles for burns 52 and 53 are shown in Figures 6.5-143 and 6.5-144 respectively. Both profiles showed a large jump from port one to the peak at sample port two.

Fraction oxide plots for burns 52 and 53 are shown in Figures 6.5-145 and 6.5-146 respectively. Although the fraction oxide plot for burn 52 showed a higher fraction of iron in all sizes than for burn 53, both plots were very similar. Both plots show a significant enrichment of sodium and especially potassium in the small sizes. This was likely due to alkali introduced during the caustic leach cleaning process.

FIGURE 6.5-143. - Temperature profile for burn 52, Gravimelt 7A.

FIGURE 6.5-144. - Temperature profile for burn 53, Gravimelt 7A.

FIGURE 6.5-145. - Fraction oxide for burn 52 at 1.9 kg/hr.

Run 53 7A Kentucky No 9

FIGURE 6.5-146. - Fraction oxide for burn 53 at 1.8 kg/hr.

Figures 6.5-147 and 6.5-148 showed ash concentrations in mg/sm^3 for burns 52 and 53 respectively. Although there are slight differences in the distribution of sampled mass, the same general trend for burns 52 and 53 was noted: the largest fraction of mass was found on stage 1. This was also true for the parent coal (Subsections 6.5.1.3 and 6.5.2.1). Although a large fraction of alkali appeared in the small sizes, the total ash concentration for the cleaned coal was significantly lower than for the parent coal. The total filter ash concentration was approximately an order of magnitude lower for the cleaned 7A.

6.5.5.3 Kentucky 9 - Eagle Butte Blend Burns

In order to fulfill the requirements of this project, a pair of experiments were performed utilizing a blend of two of the study coals, Kentucky 9 and Eagle Butte. This blend was 70% Eagle Butte and 30% Kentucky 9. In both experiments, Run 59 and Run 60, the coal was combusted at a stoichiometric ratio of 1.35 and a feed rate of 1.8. The measured NO concentrations were 535 and 602.5 ppm for Runs 59 and 60 respectively. Due to the relatively low feed rate, the temperature profile in the furnace was somewhat depressed (Figures 6.5-149 and 6.5-150). Ash samples were collected as described in Subsection 6.1.5 and analyzed by Atomic Absorption/Emission. The fraction oxide plots for these two burns can be seen in Figures 6.5-151 and 6.5-152. These plots are very similar, and would suggest that the burns were fairly reproducible. In addition, there seems to be no evidence of a enrichment of alkalis in the fume (AF), although there is a slight enrichment on plate 8 (d_{p50} 0.65 μm). Samples for Mössbauer/CCSEM analysis were also collected, but the analysis has not been performed to date.

FIGURE 6.5-147. - Ash concentration for burn 52.

FIGURE 6.5-148. - Ash concentration for burn 53.

FIGURE 6.5-149. - Uncorrected temperature profile for run 59; Kentucky 9 - Eagle Butte Blend

FIGURE 6.5-150. - Uncorrected temperature profile for run 60; Kentucky 9 - Eagle Butte Blend

FIGURE 6.5-151. - Fraction oxide versus impactor stage for run 59; Kentucky 9 - Eagle Butte Blend

FIGURE 6.5-152. - Fraction oxide versus impactor stage for run 60; Kentucky 9 - Eagle Butte Blend

6.5.6 CCSEM Results

Results of impactor samples acquired for atomic absorbance (AA) analysis were presented in Subsections 6.5.1 through 6.5.5. AA analysis gave bulk composition information for each impactor plate from which the fraction oxide plots were constructed. Subsection 6.5.6 discusses results of impactor samples subjected to computer controlled scanning electron micrography analysis (CCSEM).

CCSEM analysis was performed at the University of Kentucky on impactor samples acquired at the University of Arizona (Huffman et al. (1984)). A short discussion of analysis methodology attributable to the University of Kentucky group is presented here.

The CCSEM technique supplies fly ash composition on a particle by particle basis. An advantage of this technique is that specific inorganic matter interactions can be exposed. For example, a large number of particles at a distinct composition might suggest a specific chemical reaction product. This information would be difficult to elucidate from bulk analysis supplied by AA analysis. Unfortunately some compositions could not be fully disclosed. Some elements (e.g., carbon, oxygen, and hydrogen) could not be evaluated which leads to some uncertainty in identification of fly ash products.

6.5.6.1 CCSEM Methodology

Preparation of fly ash samples subjected to CCSEM analysis included sample mounting in an epoxy medium. The sample was then sectioned and polished prior to analysis. The technique used back-scattered electron intensity to distinguish between fly ash particles and background mounting medium. Cross-sections of fly ash particles were sized and compositions were measured. Elemental compositions were determined by centering the electron beam on a fly ash particle and collecting an energy dispersive x-ray (EDX) spectrum for approximately 2s. Analysis of over 1000 particles in each sectioned fly ash sample provided a representative of fly ash particle compositions.

6.5.6.2 Technique for Presentation of CCSEM Results

CCSEM results for each fly ash sample involved a large amount of information (Appendices H and I). Presentation of all the information in a few clear plots proved difficult. Plots of one elemental composition versus another in two dimensional plots introduces significant ambiguities. Two dimensions alone might lead the reader to assume that the composition of one particle was weighted as much as a composition that occurred for a much larger number of particles. This was also true of ternary diagrams. Ternary diagrams had the additional disadvantage that information could be lost since fly ash particles generally contained more than three constituents. For these reasons, three dimensional plots were used to present CCSEM information.

Each three dimensional plot presented in this section included a large amount of information which requires a short explanation. Composition information was presented on

the X and Y axes. Frequency of occurrence was shown on the Z axis. Only two elements were presented at one time. Figure 6.5-153 shows the two dimensional base of a typical three dimensional plot. Since compositions could not sum to greater than 100%, the region above the dashed diagonal line was "forbidden". The distance from the diagonal, *a*, was the percentage composition not included in X and Y.

Specific types of changes in compositions from a parent mineral to those measured by CCSEM could also be noted. For example, a mineral with initial composition X could be changed only due to the addition of Y. This change would be noted as a shift in X to lesser values parallel to the dashed diagonal in Figure 6.5-153. Changes of another type could be attributed to addition of species other than X or Y by movement away from dashed diagonal towards the origin.

To be complete, a large number of figures would be required. For brevity, only figures required to address a specific issue were included. Data utilized in constructing three dimensional plots are listed in Appendix H and Appendix I showed a more complete set of figures.

Although fly ash samples were acquired on all impactor stages and the after-filter, in some cases insufficient sample mass on lower stages prevented analysis. For this reason, impactor stages with sizes smaller than stage 1 were not analyzed for the bituminous coals. Table 6.5-3 shows the burn, coal, and impactor samples analyzed by CCSEM.

FIGURE 6.5-153. - Base of typical 3D plot.

TABLE 6.5-3. - List of samples analyzed by CCSEM

Burn	Coal	Impactor Samples Analyzed
21	Illinois No. 6	1
22	Beulah Lignite	1, 3, 5, 7
23	Eagle Butte	1, 5
24	Kentucky No. 9	1
27	Kentucky No. 11	1
32	Upper Freeport	1

6.5.6.3 Presentation of CCSEM Analysis Results

Presentation of CCSEM analysis results was split into two groupings that could be characterized by coal rank. The four bituminous coals (Kentucky No. 11, Kentucky No. 9, Upper Freeport, and Illinois No. 6) showed remarkably similar results and were grouped together. The two lower rank coals, Eagle Butte and Beulah Lignite, showed comparable results and were also grouped together.

6.5.6.3.1 Bituminous Coals

CCSEM results for four bituminous coals were obtained only for impactor plate 1. This was due to low mass loading in the small sizes. Subsection 6.5.4.1 showed that approximately 90% of the sampled mass in the impactor for Illinois No. 6 was found on stage 1.

Results for all four bituminous coals were extraordinarily similar. This was especially true for Kentucky No. 11, Kentucky No. 9 and Upper Freeport whose parent coals had similar mineralogies (Sections 3 and 4). Although results for Illinois No. 6 were slightly different, similarity to the other three bituminous coals analyzed was remarkable. Since results were similar for all four coals and Illinois No. 6 parent coal had a higher sodium loading than the other three, results for the bituminous coals were illustrated by Illinois No. 6.

Mineralogical results (Sections 3 and 4) showed that all four bituminous coals had a relatively high occurrence of quartz, illite, mixed silicates, and pyrite. Illinois No. 6 had a higher occurrence of calcium-rich minerals and sodium than the other three bituminous coals. Illinois No. 6 had 2260 ppm acid soluble sodium compared to 1120 ppm sodium found in the ash analysis. This suggested that most, if not all, the sodium was easily vaporized, some of which was likely lost during ashing. A similar calculation for calcium suggested that nearly

all the calcium in the parent coal was calcite not found in the other three bituminous coals. Approximately 80% of calcite in the parent coal was 10 μm or larger. Illinois No. 6 had a higher ratio of CaO and Na_2O to the sum of Al_2O_3 and SiO_2 than the other three bituminous coals, and also a lower ash loading (9.9% DB compared to 15 to 24%).

Figure 6.5-154 shows CCSEM results for Al versus Si for Illinois No. 6 impactor plate 1. The frequency of occurrence of a particular composition (Si, Al) was represented by the height on the Z axis. A large peak at (100, 0) suggested chemically unchanged quartz which was approximately 20% of the mineral matter in the parent coal. A larger peak of nearly all Al and Si was located at approximately (60, 30). This peak was attributable to illite and miscellaneous silicates which were 10 and 18% of the parent coal mineral matter respectively. A lower ridge from (0,0) to the illite peak was likely the result of illite and miscellaneous silicates reacting, coagulating, or agglomerating with other species like calcium, iron, and sodium.

These observations were noted in the other three bituminous coals. A smaller peak at approximately (45, 55) was also noted for all four coals. Although relative peak heights differed slightly for the four coals, no significant differences in compositions were noted.

FIGURE 6.5-154. - Al versus Si Illinois No. 6 impactor 1.

The calcium versus silicon (Si, Ca) plot shown in Figure 6.5-155 suggested that there were some particles that contained a large fraction of calcium and no silicon. This might be attributable to calcite in the parent coal and was sometimes associated with sulfur. The other three bituminous coals, however showed a more pronounced peak at compositions $> 90\%$ Ca and no calcite was reported in the parent coal. The illite peak (Si = 60) showed a slight contamination of calcium. It was interesting to note a small peak for all four coals at an approximate composition of (30, 50). This was noted to a significant extent for the lower rank coals discussed in the next section.

Iron versus silicon (Si, Fe) is shown in Figure 6.5-156. The results were similar to the calcium results with a peak at (0, 100) likely due to extraneous oxidized pyrite. Some contamination of the illite peak with iron was noted and so was a slight peak at approximately (30, 55). This latter peak was noted for all four bituminous coals. However, this peak was not noted for the lower rank coals with the exception of a slight peak for impactor stage 1 for Beulah Lignite.

Sodium versus silicon is shown in Figure 6.5-157 in which the direction from which the plot is viewed has been reversed with respect to previous CCSEM plots. This plot shows

FIGURE 6.5-155. - Ca versus Si Illinois No. 6 impactor 1.

FIGURE 6.5-156. - Fe versus Si Illinois No. 6 impactor 1.

FIGURE 6.5-157. - Na versus Si Illinois No. 6 impactor 1.

that the majority of particles analyzed contained no sodium. Sodium present was associated with a fairly specific stoichiometry which indicated a possible reaction product. The composition suggested that sodium may have reacted with aluminosilicates having a composition similar to the illite peak. An analogous reaction peak with quartz was not evident.

Illite comprised approximately 10% of the mineral matter in the parent coal. The parent illite contained 13% potassium. Miscellaneous silicates (18% of parent mineral matter) had a higher Si-to-Al ratio than illite and was approximately 10% potassium. In contrast, the CCSEM results shown in Figure 6.5-158 show that less than 2% of the particles measured on plate 1 had a potassium composition of 10% or higher. This suggested that a fraction of the potassium originally bound in the mineral matter was released.

6.5.6.3.2. Low Rank Coals

Contrary to the bituminous coals (Subsection 6.5.6.3.1), two low rank coals (Eagle Butte and Beulah Lignite) had enough fly ash mass in smaller sizes for CCSEM analysis. The original mineral matter and CCSEM results for these two coals were sufficiently different from the bituminous coals to warrant a separate discussion.

FIGURE 6.5-158. - K versus Si Illinois No. 6 impactor 1.

The Al versus Si plot for Eagle Butte impactor plate 1 showed almost no pure Al plus Si particles with the exception of quartz (Appendix I). This suggested that all the aluminosilicate clays were transformed by some mechanism during combustion. On the other hand, CCSEM results for Beulah Lignite impactor plate 1 (Figure 6.5-159) showed a peak corresponding to a composition of nearly all silicon (93, 2), and another of nearly all Al plus Si (56, 30). These were most likely quartz and kaolinite respectively which had undergone only a slight change during combustion. A large ridge from (0, 0) to (56, 30) with a large peak at (23, 16) suggested significant transformations of kaolinite during combustion. Some small peaks on the X axis other than (93, 2) suggested altered quartz. This implied that while some minerals were only slightly affected or altered during combustion some of the same types of minerals were greatly affected.

Comparison of Al versus Si for impactor plate 1 to impactor plates 3, 5, and 7 (Figures 6.5-160 to 6.5-162) showed that the fraction of quartz and clay that was unaffected decreased as size decreased. Plates 5 and 7 showed no unaffected quartz or clays. This was consistent with the results for Eagle Butte plate 5.

The observation of existence of both transformed and unaltered silicates in the large sizes might be attributable to the original form of the mineral matter. Close proximity and opportunity for coalescence of included mineral matter would increase the probability of transformation relative to the extraneous mineral matter.

FIGURE 6.5-159. - Al versus Si Beulah Lignite impactor 1.

FIGURE 6.5-160. - Al versus Si Beulah Lignite Impactor 3.

FIGURE 6.5-161. - Al versus Si Beulah Lignite Impactor 5.

FIGURE 6.5-162. - Al versus Si Beulah Lignite Impactor 7.

Figures 6.5-163 to 6.5-166 showed that a primary transformation of clays was due to Ca. In all four size classes (impactor plates 1, 3, 5, and 7) the most frequent composition noted was rich in Ca. Mineralogical analysis (Sections 3 and 4) showed clay as a significant portion of the mineral matter (kaolinite 30% and other aluminosilicates 15%). The ratio of Si-to-Al for kaolinite in the parent coal was approximately 1.24 and for the other aluminosilicates it was 1.96. The composition of the largest peak in all four sizes was shown in Table 6.5-4, and was likely a reaction product of calcium with kaolinite as noted by the relatively specific composition.

The sum of three major species (Ca, Al, and Si) decreased as size decreased due to increases in other species. Relatively larger changes were observed in the less massive smaller sizes. A peak shown in Figure 6.5-163 was nearly "pure" calcium (likely CaO). The calcium peak decreased with size and did not appear for impactor plates 5 and 7. These results are discussed further in Subsection 6.6.4.

Both Eagle Butte and Beulah Lignite showed small peaks of "pure" iron in the largest size class. These particles did not exist in smaller size classes and were likely due to oxidized extraneous pyrite particles. Few aluminosilicate fly ash particles showed high iron concentrations and no relatively specific composition was apparent. This suggested that Fe associated with Si was due to agglomeration or coagulation between iron and aluminosilicate particles.

FIGURE 6.5-163. - Ca versus Si Beulah Lignite Impactor 1.

FIGURE 6.5-164. - Ca versus Si Beulah Lignite Impactor 3.

FIGURE 6.5-165. - Ca versus Si Beulah Lignite Impactor 5.

FIGURE 6.5-166. - Ca Versus Si Beulah Lignite Impactor 7.

TABLE 6.5-4. - Most frequent composition in Beulah Lignite fly ash

Impactor Plate	Elemental Composition			Ratio Si/Al	Ratio Si/Ca
	Ca	Al	Si		
1	53	16	23	1.44	0.43
3	44	17	23	1.35	0.52
5	40	17	22	1.29	0.55
7	39	11	15	1.36	0.38

In the large size classes, where condensation would affect the overall composition only slightly, both Eagle Butte and Beulah Lignite showed relatively specific compositions in the plots of sodium versus silicon. The results for Eagle Butte impactor plates 1 and 5 are shown in Figures 6.5-167 and 6.5-168. Beulah Lignite results for plates 1, 3, 5, and 7 are shown in Figures 6.5-169 through 6.5-172. As particle size decreased, the specific composition became less evident due to condensation of vaporized alkali on smaller particles.

Both quartz and kaolinite appear to have reacted with sodium. Comparisons of Na versus Su, Ca versus Si, and Na versus Ca plots showed that, with the exception of the largest peak, Na and Ca existed together. This implied that the reaction of sodium with silicates might be competing with calcium.

The behavior of potassium in both Beulah Lignite and Eagle Butte was difficult to discern. Both coals had a relatively low illite concentration of 1 and 2% of the mineral matter respectively. The concentration of potassium in illite for Beulah Lignite was approximately 8% and for Eagle Butte 10%. Very few particles showed concentration levels as high or higher than these values. Lowering of potassium levels however, might be due to condensation or coagulation with non-potassium species.

Although calcium existed relatively often in particles of nearly all calcium, magnesium did not. Calcium also existed in particles that contained no magnesium. However, for all the Beulah Lignite fly ash particles and nearly all the Eagle Butte particles, magnesium was associated with particles that were relatively rich in calcium. The reason for the magnesium appearing with calcium rich particles is discussed somewhat in Subsection 6.6.4.

Single particle compositions (wt%) are shown in Figures 6.5-173 and 6.5-174 for Loy Yang 2301 doped with kaolinite. These CCSEM of ash trap samples show extraneous kaolinite has captured sodium to form nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

FIGURE 6.5-167. - Na versus Si Eagle Butte Impactor 1.

FIGURE 6.5-168. - Na versus Si for Eagle Butte Impactor 5.

FIGURE 6.5-169. - Na versus Si Beulah Lignite Impactor 1.

FIGURE 6.5-170. - Na versus Si Beulah Lignite Impactor 3.

FIGURE 6.5-171. - Na versus Si Beulah Lignite Impactor 5.

FIGURE 6.5-172. - Na versus Si Beulah Lignite Impactor 7.

FIGURE 6.5-173. - Loy Yang 2301 + kaolinite, Al+Si+Na > 80%, dp > 10 μ m.

FIGURE 6.5-174. - Loy Yang 2301 + kaolinite, Al+Si+Na > 80%, dp < 10 μ m.

6.6 Analysis - Alkali Behavior

The previous sections presented results of experimental efforts studying mineral matter transformations during pulverized coal combustion. A brief discussion of experimental results and noteworthy trends was included. A more detailed and encompassing discussion of results related to the fate of alkali species is the purpose of Subsection 6.6.

Subsection 6.6.1 presents results and discussion of equilibrium calculations. Equilibrium calculations, which focussed on alkali species, were performed on both practical and surrogate coal systems. Several observations in Subsection 6.5 showed sodium vaporization as a notable mechanism. Capture of sodium by silicates was also prominent. These mechanisms are discussed in more detail in Subsection 6.6.2. Sodium is generally considered to be organically bound and hence is considered readily vaporizable during combustion. Potassium, on the other hand, is typically bound in mineral matter and is naturally involatile. Mechanisms of potassium release in the presence of sodium is discussed in Subsection 6.6.3. Highly dispersed calcium in low-rank coals formed large ($> 10 \mu\text{m}$) calcite particles. Transformation of dispersed calcium is the topic of Subsection 6.6.4.

6.6.1 The Behavior of Alkali in a Coal Combustion Environment at Equilibrium

Thermodynamic equilibrium is a limiting case that can provide some insight into behavior of chemically reacting systems. Unfortunately, application of equilibrium calculations to mineral matter might be misleading when applied to systems with relatively short time scales such as combustion systems. Relatively slow transport mechanisms of mineral matter compared to combustion time scales does not allow for equilibrium to be attained. It has been shown however, that gas phase reactions of sodium species are fast compared to time scales in a combustor and equilibrium might be applicable at least with respect to the gas phase (Srinivasachar, et al. (1990), Boni, et al. (1990)). Some insight might also be gained through equilibrium calculations concerning alkali behavior relative to condensed phases. A study was undertaken to determine the behavior of sodium and potassium at equilibrium in practical and surrogate coal systems. The surrogate coal system studied matrix effects of various species (eg. chlorine and sulfur) on alkali behavior.

The NASA CET86 program (Gordon and McBride (1986)) was used for equilibrium calculations. Of primary interest was the form of the alkalis sodium and potassium. To focus on Na and K interactions, and to ensure a wide temperature range for computer program conversion, Ca, Mg, and Fe were omitted from equilibrium calculations. Alkali species considered by the program were included in Appendix G. It is suspected that Ca, Mg, and Fe would affect alkali behavior primarily through competition for silicates. Formation of calcium silicate, for example, would allow less alkali silicate formation. Omitting Ca, Mg, and Fe allowed for a greater temperature range of successful conversion of the numerical technique. For practical coal systems (Subsection 6.6.1.1) calculations were performed with Ca, Mg, and Fe omitted and the ash normalized to the remaining species: Si, Al, Na, K, S, and Cl. The fraction of ash in the parent coal was unaltered. Moisture in the coal was divided into its constituents, H and O, and added to respective components of the

ultimate analysis. Table 6.6-1 shows coal compositions used for calculations on the base suite of coals.

Subsection 6.6.1.2 discusses results from calculations with surrogate coal systems. Surrogate coal was used to study effects of various species and relative compositions on behavior of both Na and K. In addition to effects of Cl and S, effects of each of the alkalis on the other was also studied.

TABLE 6.6-1. Coal compositions for equilibrium calculations on the base suite of coals

wt% As-received	Upper Freeport	Kentucky No. 11	Kentucky No. 9	Illinois No. 6	Beulah Lignite	Eagle Butte	Loy Yang 2301	Loy Yang 1953
C	64.57	59.98	58.06	59.87	58.96	50.26	58.96	43.97
H	4.13	5.20	4.86	6.04	6.30	6.59	5.66	6.65
O	4.37	15.31	11.31	20.34	40.62	36.98	33.03	46.50
N	1.63	1.63	1.18	1.37	0.82	1.01	0.46	0.58
S	2.07	3.55	4.30	3.76	1.31	0.34	0.26	0.27
SiO ₂	14.51	8.71	12.76	5.53	3.28	2.29	0.23	0.36
Al ₂ O ₃	7.06	4.02	5.30	2.16	2.20	1.25	0.06	0.16
Na ₂ O	0.09	0.18	0.08	0.16	0.03	0.16	0.87	0.41
K ₂ O	0.89	0.51	0.70	0.25	0.05	0.02	0.01*	0.02
SO ₃	0.69	0.92	1.45	0.53	3.20	1.10	0	0.80
Cl	NA	NA	NA	NA	NA	0	0.95	0.25
* Analysis was <0.01% dB								

6.6.1.1 Practical Coal Systems

6.6.1.1.1 Base Suite of Coals

Results for each coal in the base suite are shown in Figures 6.6-1 through 6.6-16. Compositions for each alkali are presented as mole fractions of all species containing that alkali. Open symbols are for vapor species and filled symbols are for condensed species.

Results for Upper Freeport, Kentucky No. 11, Kentucky No. 9, and Illinois No. 6 were all similar. For these coals, the major vapor species were elemental Na above 1600 K and NaOH above 1200 K. NaOH was the dominant vapor species. Na₂SO₄ existed in the vapor in a relatively narrow temperature range from 1100 to 1500 K.

FIGURE 6.6-1. - Results for sodium in Upper Freeport

FIGURE 6.6-2. - Results for potassium in Upper Freeport

FIGURE 6.6-3. - Results for sodium in Kentucky No. 11

FIGURE 6.6-4. - Results for potassium in Kentucky No. 11.

FIGURE 6.6-5. - Results for sodium in Kentucky No. 9.

FIGURE 6.6-6. - Results for potassium in Kentucky No. 9.

FIGURE 6.6-7. - Results for sodium in Illinois No. 6.

FIGURE 6.6-8. - Results for potassium in Illinois No. 6.

FIGURE 6.6-9. - Results for sodium in Beulah Lignite.

FIGURE 6.6-10. - Results for potassium in Beulah Lignite.

FIGURE 6.6-11. - Results for sodium in Eagle Butte.

FIGURE 6.6-12. - Results for potassium in Eagle Butte.

FIGURE 6.6-13. - Results for sodium in Loy Yang 2301.

FIGURE 6.6-14. - Results for potassium in Loy Yang 2301.

FIGURE 6.6-15. - Results for sodium in Loy Yang 1953.

FIGURE 6.6-16. - Results for potassium in Loy Yang 1953.

Condensed species, that could be possible reaction products of sodium with silicates, returned by the equilibrium program were $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$ (albite?) (between 1000 and 1400 K) and $\text{Na}_2\text{Si}_2\text{O}_5$ (between 1200 and 1700 K). $\text{Na}_2\text{SO}_4(l)$ existed in only a very narrow temperature range around 1300 K. $\text{Na}_2\text{SO}_4(s)$ existed below 1100 K. These results were consistent with those of Srinivasachar et al. (1990a), and Steinberg and Schofield (1990). Both references claimed that $\text{Na}_2\text{SO}_4(v)$ was not an important species above 1650 K and may appear on boiler tubes at those temperatures due to heterogenous reaction.

Potassium results showed that KOH was the dominant vapor species above 1400 K. Elemental K contributed to the vapor above 1700 K. Between approximately 1200 and 2000 K $\text{K}_2\text{Si}_4\text{O}_9$ was the major condensed species. Below 1200 K K_2SO_4 was the primary condensed species.

For Beulah lignite the results for both Na and K were similar to the four bituminous coals discussed above with some minor differences. A larger fraction of Na was in a condensed phase at higher temperatures for the Beulah Lignite compared to the bituminous coals. The converse was true for K which showed a larger fraction in the vapor for Beulah Lignite.

The Na results for Eagle butte were somewhat similar to the bituminous coals. K results however, were different from the four bituminous coals discussed above: the Eagle Butte results did not show $\text{K}_2\text{Si}_4\text{O}_9$ as a condensed phase. This could be due to the low silicate content and competition with Na.

The two Loy Yang coals were different from the six coals discussed above due to their low ash, relatively high sodium to silicate ratio, and also due to Cl present. Due to low concentrations Cl was neglected in equilibrium calculations for the other six coals. Alkali behavior in the presence of Cl can be deduced from Loy Yang and surrogate coals. Cl caused significant differences for the two Loy Yang coals in comparison to those discussed previously in the absence of Cl. For Loy Yang 2301, elemental Na was still found above 1600 K, but NaCl (found above 900 K) was the dominant vapor species. NaOH was still a significant vapor species above 1300 K. It was interesting to note that although Na_2SO_4 was not an important vapor species, it was an important condensed species below 1500 K. NaCl was also an important condensed species below 1100 K. Two solid phases of $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{16}$, and both liquid and solid $\text{Na}_2\text{Si}_2\text{O}_5$ were important condensed phases below 1900 K. Potassium was primarily in the vapor above 900 K as either KCl (900 to 2000 K) or KOH (above 1300 K).

Sodium results for Loy Yang 1953 were similar to those for Loy Yang 2301 except there were more condensed species and NaCl vapor did not appear below 1100 K. KOH was more prevalent for Loy Yang 1953 than for Loy Yang 2301. Condensed K_2SO_4 below 1300 K also was present for Loy Yang 1953 whereas Loy Yang 2301 did not have a condensed potassium phase.

6.6.1.1.2 Cleaned Coals and Doped Coals

In addition to the base suite, two cleaned coals and two doped coals were also included in this study. Wider variation in coal and ash compositions gave interesting results. Table 6.6-2 gives coal compositions used for equilibrium calculations. Compositions were calculated from parent coals using the assumptions stated in the introduction of Subsection 6.6.1.

TABLE 6.6-2. Coal compositions for equilibrium calculation on the cleaned and doped coals

wt% as-received	Illinois No. 6 SOAP	Kentucky No. 9 7A	Kent No. 11 + NaAc	LY 2301 + Kaolin
C	57.83	65.18	56.17	53.90
H	6.62	4.43	5.33	5.41
O	29.36	27.92	18.69	32.06
N	1.11	1.65	1.48	0.43
S	2.22	0.60	3.23	0.24
SiO ₂	1.70	0.23	8.55	3.89
Al ₂ O ₃	0.82	0.09	3.95	2.76
Na ₂ O	0.07	0.04	1.19	0.64
K ₂ O	0.10	0.06	0.50	0.02
SO ₃	0.15	0	0.80	0
Cl	0	0	0	0.69

Illinois No. 6 SOAP and Kentucky No. 9 7A were the cleaned coals. The ash removal process for the SOAP took advantage of the greater mineral matter density relative to the organic matter in the coal. The coal was floated on an oil that had a lower density than most of the mineral matter (and high ash coal particles). The resultant ash was expected to be primarily inherent. A caustic leach process was used for Kentucky No. 9 7A. A molten mixture of NaOH and KOH leached out a large fraction of the original mineral matter. Although the ash content of 7A was greatly reduced, ash present was relatively high in Na and K that was expected to be easily vaporized. The cleaned product might be analogous to Loy Yang except 7A had no Cl and its rank was higher.

Alkali interactions with silicates were also studied with two doped coals. Kentucky No. 11 was doped with 98.86 g sodium acetate trihydrate (NaAc) per kg coal to study effects of Na on K. Kentucky No. 11 was used due to a relatively high occurrence of illite

(potassium aluminosilicate) and low sodium content. NaAc additive gave a similar sodium-to-silicate ratio as Beulah Lignite. Capture of sodium by extraneous silicate was studied by doping Loy Yang 2301 with 94 g kaolinite per kg coal. Loy Yang was used due to a relatively high sodium-to-silicate ratio. The kaolinite additive gave a comparable sodium-to-silicate ratio as Beulah Lignite. Results for the four coals are shown in Figures 6.6-17 through 6.6-24.

Although the ash content was much lower for Illinois No. 6 SOAP in comparison to the parent Illinois No. 6 discussed above, equilibrium calculations for sodium and potassium were similar. The SOAP, however showed slightly more vapor K species above 1400 K than the parent coal.

Both Na and K results for the Kentucky No. 9 7A were similar to the parent coal (Kentucky No. 9). The major difference was more of both alkalis was calculated to be in the vapor for the 7A above 1400 K.

It was interesting to note that a greater fraction of Na was as $\text{Na}_2\text{Si}_2\text{O}_5$ in the Kentucky No. 11 doped with NaAc compared to the parent Kentucky No. 11. The K results for the doped coal did not differ significantly from the parent coal.

FIGURE 6.6-17. - Sodium species in Illinois No. 6 SOAP.

FIGURE 6.6-18. - Potassium species in Illinois #6 SOAP.

FIGURE 6.6-19. - Sodium species in Kentucky No. 9 7A.

FIGURE 6.6-20. - Potassium species in Kentucky No. 9 7A.

FIGURE 6.6-21. - Sodium species in Kentucky #11 + NaAc.

FIGURE 6.6-22. - Potassium species in Kent #11 + NaAc.

FIGURE 6.6-23. - Sodium in Loy Yang 2301 + kaolinite.

FIGURE 6.6-24. - Potassium in Loy Yang 2301 + kaolinite.

Addition of kaolinite to Loy Yang 2301 had significant effects on the equilibrium state of Na. The lower limit for elemental Na in the vapor moved from 1400 K to 1500 K and there was less vapor Na for the Loy Yang doped with kaolinite compared to the parent coal. Also, the fraction of Na as sodium silicates below 1500 K was higher for the doped coal. Below 1400 K condensed K_2SO_4 was an important constituent of the doped Loy Yang whereas all the K was in the vapor for the undoped Loy Yang 2301.

6.6.1.2 Surrogate Coal Systems

Equilibrium calculations using surrogate coal compositions were performed in an attempt to better understand affects and interactions of various species on alkali behavior. In this study, a focus was placed on K, Na, Cl, and S. Silica and alumina were also included in a 2:1 ratio. This ratio and the surrogate coal compositions might be considered typical when compared to practical coal systems shown in Table 6.6-3. Table 6.6-3 shows the surrogate coal compositions.

For surrogate coals, H, O (not in the ash) and N compositions were held constant. As ash content was increased, carbon content was decreased to compensate. Results were presented as mole fraction of elemental alkali in the vapor, not to be confused with Figures 6.6-1 to 6.6-24 which showed mole fraction of alkali-containing species (e.g., NaOH and Na_2SO_4).

TABLE 6.6-3. Coal compositions for surrogate coal systems

wt%	C	H	O	N	(Ash)	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	SO ₃	Cl
Na	60	6	20	1	13	8	4	1	0	0	0
Na,K	59	6	20	1	14	8	4	1	1	0	0
Na,S	59	6	20	1	14	8	4	1	0	1	0
Na,3S	57	6	20	1	16	8	4	1	0	3	0
Na,Cl	59	6	20	1	14	8	4	1	0	0	1
Na,3Cl	57	6	20	1	16	8	4	1	0	0	3
Na,K,S	58	6	20	1	15	8	4	1	1	1	0
Na,K,Cl	58	6	20	1	15	8	4	1	1	0	1
Na,S,Cl	58	6	20	1	15	8	4	1	0	1	1
Na,K,S,Cl	57	6	20	1	16	8	4	1	1	1	1
Na,3K	57	6	20	1	16	8	4	1	3	0	0
Na,6K	54	6	20	1	19	8	4	1	6	0	0
K	60	6	20	1	13	8	4	0	1	0	0
K,S	59	6	20	1	14	8	4	0	1	1	0
K,3S	57	6	20	1	16	8	4	0	1	3	0
K,Cl	59	6	20	1	14	8	4	0	1	0	1
K,3Cl	57	6	20	1	16	8	4	0	1	0	3
K,S,Cl	58	6	20	1	15	8	4	0	1	1	1
K,3Na	57	6	20	1	16	8	4	3	1	0	0
K,6Na	54	6	20	1	19	8	4	6	1	0	0
K	66	6	20	1	7	4	2	0	1	0	0
K,Na	65	6	20	1	8	4	2	1	1	0	0
K,3Na	63	6	20	1	10	4	2	3	1	0	0
K,6Na	60	6	20	1	13	4	2	6	1	0	0

Figure 6.6-25 shows the mole fraction of Na in the vapor for five different surrogate coal compositions. Figure 6.6-25 showed that S had an insignificant effect on the fraction of Na that appeared in the vapor phase. However, as results on practical coal systems showed, S could have a significant affect on the form of condensed Na. Cl showed a dramatic effect on the fate of Na. Addition of Cl increased the fraction of Na in the vapor. Subsequent addition of K to the system significantly lowered the fraction of Na in the vapor that was caused by the addition of Cl. This, in part, showed the importance of Cl on the K behavior.

Figure 6.6-26 shows the effect of K on the fraction of Na in the vapor for a system with lower silica and alumina content. The Na behavior appeared to be unaffected until the ratio of potassium oxide to sodium oxide in the ash (K/Na) reached approximately 3. Above a K/Na ratio of 3 addition of potassium to the system increased the fraction of Na in the vapor. The point at which the fraction of Na in the vapor began to increase significantly with K/Na ratio a function of the ratio of sodium oxide to silica and alumina (Na/SiAl). As Na/SiAl increased, the point at which the fraction of Na in the vapor was affected by K/Na ratio decreased. Apparently the silicates reach a saturation of alkali.

FIGURE 6.6-25. - Evolution of sodium with K, Cl, and S.

FIGURE 6-6-26. - Effect of potassium on sodium.

Figure 6.6-27 shows that the effect of S on the behavior of K is similar to that for Na. S did not significantly alter the fraction of K in the vapor. As with Na however, previous equilibrium calculations on practical coal systems showed that S could significantly affect the condensed form of potassium. In contrast to sodium results (Figure 6.6-25) only a small amount of Cl was required to force all the potassium into the vapor phase. Addition of Na to the K-Cl system reduced the fraction of K in the vapor, but not as much as the reduction of Na in the vapor due to the addition of K to the Na-Cl system. It appears that Cl has a higher affinity for K than Na, and KCl vapor is more stable than NaCl. Cl had a more marked effect on the behavior of K than on the behavior of Na. However, effects of Cl on the behavior of both alkalis were found to be significant.

Figures 6.6-28 and 6.6-29 show the effect of Na on K behavior. In Figure 6.6-28 the ratio of potassium oxide to silica plus alumina (K/SiAl) was 1/12. The ratio of sodium oxide to potassium oxide (Na/K) had to be greater than 1 for the K behavior to be significantly altered. For temperatures greater than 1500 K, all of the potassium was in the vapor phase for Na/K set to 6. In Figure 6.6-29 K/SiAl was 1/6 and all of the potassium was in the vapor phase above 1500 K for Na/K set to 3, and above 1400 K for Na/K set to 6. The ratio Na/K where the K behavior was significantly affected decreased as the ratio K/SiAl increased. This was similar to the effects of K on Na behavior, however the effects of Na on K behavior were greater for similar compositions.

FIGURE 6.6-27. - Evolution of K with Na, Cl, and S.

FIGURE 6.6-28. - Effect of sodium on potassium.

FIGURE 6.6-29. - Effect of sodium on potassium, low aluminosilicates.

6.6.1.3 Conclusions

- For the practical coal systems used in this equilibrium study, NaOH was found to be the primary Na vapor species in the absence of Cl. Mole fractions of NaOH and NaCl were nearly the same at temperatures above 1800 K in the Loy Yang 1953 system. NaCl was the dominant vapor species for Loy Yang 2301, Loy Yang 2301 doped with kaolinite, and Loy Yang 1953 below 1800 K. NaOH was still a significant species in the Loy Yang 2301 system above 1400 K. Elemental Na was significant in the vapor phase only above 1600 K.
- A major condensed species in the temperature range between approximately 1100 and 1800 K was a sodium silicate $\text{Na}_2\text{Si}_2\text{O}_5$. This is a possible reaction product of sodium with quartz which is a common impurity in coal systems. A sodium aluminosilicate was formed between 1000 and 1400 K. It should be noted that the known reaction product, nepheline ($\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$), was not included in the program data base (Appendix 6.I).
- Na_2SO_4 was not an important vapor species but was a dominant condensed species below approximately 1100 K.
- Potassium in general behaved similarly to sodium in these systems but some important differences were present. In the absence of Cl, KOH was the major species in the vapor phase. The behavior of K in the Loy Yang systems, which contained Cl, was similar to that found for Na in those systems. Contrary to Na_2SO_4 , K_2SO_4 was a

notable vapor constituent between 1200 and 1500 K. Elemental K was a significant vapor species above approximately 1800 K.

A possible reaction product of K and quartz ($K_2Si_4O_9$) was a significant condensed species between 1100 and 1900 K. Although present only in small amounts in the vapor phase, condensed K_2SO_4 dominated the potassium compounds below 1200 K.

Study of surrogate coal systems showed that Na behavior was influenced greatest by presence of Cl. More Na was found in the vapor phase in the presence of Cl than in its absence. K affected Na behavior, but S showed a negligible influence. With respect to K influence, the relative ratio of sodium oxide to silica plus alumina (Na/AlSi) in the parent system also proved to be important. More Na was found in the vapor phase in the presence of K when the ratio Na/AlSi was higher. This could be due to a competition reaction between Na and K for the silicates.

Chlorine had a stronger influence on K behavior than for Na. Compared to Na, a smaller Cl content in the parent system was required to shift all of the K to the vapor phase. Sulfur showed a negligible influence, but Na had a significant affect on K behavior.

Na showed a greater affect on K than the reverse. The extent of the effect of Na on K behavior was a function of the ratio of potassium oxide to silica plus alumina (K/SiAl). More K was found in the vapor phase for a higher K/SiAl ratio at the same Na loading. As was discussed with Na, this could be due to a competition reaction between Na and K for the silicates. Silicate affinity for Na appears to be higher than that for K. Higher loadings of Na could allow all of the K to exist in the vapor phase above 1500 K.

6.6.2 Mechanisms Governing Sodium Transformations During Pulverized Fuel Combustion

A significant fraction of sodium in coal is known to vaporize during combustion (Wibberly and Wall (1982a,b), Punjak et al. (1989), Uberoi et al. (1990), Srinivasachar et al. (1990a)). Vapor sodium can contribute to metals corrosion and ceramics devitrification in combustion systems (Hastie et al. (1982)). Condensation of vapor sodium is the cause of sodium enrichment in boiler tube deposits (Scandrett and Clift (1984)) and also enrichment of sodium in submicron particles (Neville and Sarofim (1985), Quann et al. (1990)). Submicron fly ash is an environmental and health concern since this size range is easily respirable (Lodge and Chan (1986)).

Fraction oxide plots in this study (Subsection 6.5) showed evidence that a significant fraction of sodium present in coal vaporized during combustion. This was shown in the marked enrichment of alkali in the small sizes for coals like Beulah Lignite and Loy Yang. Results of CCSEM analysis also showed that sodium chemically reacted with silicates. These data suggested that sodium transformations are dictated by its original form in the parent coal and its chemical and physical interactions with other ash constituents.

Subsection 6.6.2 is divided into subsections which describe sodium behavior during pulverized coal combustion. The original form and occurrence of sodium in coal, discussed in Subsection 6.6.2.1, dictates its vaporization characteristics (Subsection 6.6.2.2). Sodium gas phase chemistry (Subsection 6.6.2.3) dictates its behavior in the hot post flame region including high temperature interactions with silicates (Subsection 6.6.2.4). Finally, condensation of sodium on existing fly ash particles in cooler regions of combustion systems is discussed in Subsection 6.6.2.5.

6.6.2.1 The Mode and Occurrence of Sodium in Coal

In the base suite of coals used in this study, the sodium composition ranged from a low of approximately 600 ppm (DB) for Kentucky No. 11 to 8400 ppm for Beulah Lignite. A typical range might be 200 to 700 ppm (Neville and Sarofim (1985)). Sodium oxide in ash ranged from 0.3 wt% (Kentucky No. 11) and 6.1 wt% (Beulah Lignite) to a high of 27 wt% for Loy Yang 2301. These values typify the range of coal and ash sodium content found in most coals (Raask (1985), Lindner (1988)).

The sodium mode of existence in coal is variable. Sodium can exist in clays such as albite ($\text{NaAlSi}_3\text{O}_8$) (Raask (1985), Lindner (1988)), plagioclase ($\text{NaCaAlSi}_x\text{O}_y$) (Srinivaschar et al. (1990a)), or in illite ($\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (perhaps substituted for potassium) or montmorillonite ($((1-x)\text{Al}_2\text{O}_3 \cdot x(\text{MgO}, \text{Na}_2\text{O}) \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O})$) (Neville and Sarofim (1985)). It is also a minor constituent in many minerals found in the base suite of coals used in this study (Sections 3 and 4). In the low-rank coals, sodium bound in clays made up only a small portion of the total sodium content. Clays accounted for a much higher percentage of sodium in higher rank bituminous coals.

Sodium can also exist in coal as organically bound to oxygen anions such as carboxylic and phenolic groups. Durie (1961) extracted Yallourn brown coal with water soluble salts and hydrochloric acid and concluded that sodium (as well as Ca and Mg) was bound to carboxylic groups in the coal matrix.

Halides are another form of sodium in coal. Caswell (1981) suggested that chlorides can associate with sodium present in inherent water. XAFS analysis of low-rank coals for this study provided an identical result (Section 4). Both the sulfate and chloride content of coals used in this study were low with Loy Yang having the highest occurrence of both anions (Sections 3 and 4).

Variability of the mode of occurrence of sodium in the coal matrix does appear to follow a general trend related to coal rank (Lindner (1988), Neville and Sarofim (1985)). In lignite and sub-bituminous coals, sodium occurs primarily associated with the organic matter (Miller and Given (1978)). In high-rank bituminous coals, sodium is associated with mineral matter such as illite and illite-montmorillonite (Gluskoter (1967), Gluskoter and Ruch (1971)). A good summary of the mode of occurrence was given by Bryers (1988) who claimed that as coalification proceeds (increasing coal rank) "chemical bonds are destroyed, and the alkali metal sodium is transformed from an organo-metallic compound to dissolved salts and eventually silicates".

Additional discussion of this topic is presented in Section 4 of this report, and in the Phase I Final Report (Boni et al., 1990).

6.6.2.2 Mechanism of Sodium Release from Coal

The mechanism of vaporization (or release) of sodium from coal is of interest when considering scavenging strategies. Sodium present in clays is not expected to contribute to the vapor form of sodium due to its low activity in silica melts (Boni et al. (1987)). Organically bound sodium and sodium salts are the primary source of sodium in the vapor phase.

Srinivasachar et al. (1990a) provided evidence that sodium in both Beulah Lignite and Loy Yang does not vaporize as $\text{NaCl}_{(v)}$. Sodium in Loy Yang may exist associated with chlorine (5100 ppm Na, 7500 ppm Cl), but in Beulah Lignite it exists primarily bound to organic matter (8400 ppm Na, 95 ppm Cl). Srinivasachar et al. showed that sodium for these two coals vaporized similarly, and at a significantly higher temperature than required for a pure NaCl source. At a heating rate of 250 K/s under an argon atmosphere they showed sodium started to be liberated from both Loy Yang and Beulah Lignite at approximately 1000°C (1273 K) and was completed just above 1700°C (1973 K). Chlorine, on the other hand, was typically liberated from British coals (high in both sodium and chlorine) at temperatures of 170°C (543 K) as HCl with no loss of sodium (Hodges et al. (1983), Pearce and Hill (1986)). Sodium and chlorine are liberated from low-rank coal separately and at markedly different temperatures. From this evidence it can be concluded that the mechanism of sodium release from low-rank coal is not vaporization of molecular sodium chloride.

Hastie et al. (1982) used benzoate salts of sodium and potassium (NaOOC_6H_5 and KOOC_6H_5) to model release of organically bound alkali in coal. They claimed that at approximately 800 K, benzoate salts decomposed to carbonate and char residue, and at temperatures of 1000 K the carbonate reacted with carbon to yield vapor alkali. With M representing alkali the sequence can be summarize by the following equations:

The second reaction was also proposed by McKee and Chatterji (1978) to account for evolution of vapor sodium above 1173 K in graphite samples doped with sodium carbonate.

Decomposition of carboxylic groups in coal to alkali carbonate was also suggested by Schafer (1979a, 1980). Schafer showed that carboxylic groups in low rank Australian coals decomposed at relatively low temperatures (below 873 K) liberating carbon dioxide. Using

brown coal ion exchanged with magnesium, Schafer (1979b) claimed decomposition of the salt form of the carboxylic acid groups initially formed the carbonate of the cation.

Schafer (1979b) also postulated that carboxyl groups were associated with other oxygen groups. This was consistent with Wigmans et al. (1983) who suggested formate structures like (A) in resonance with structure (B). Wigmans et al. worked with birchwood based Degussa activated carbon impregnated with sodium carbonate. Yuh and Wolf (1984) also suggested the formation of surface sodium oxygen complexes in coal from sodium carbonate (including (A) shown below). Yuh and Wolf claimed that in the presence of oxidizing species (like H₂O, CO and CO₂) surface sodium-oxygen complexes could transform back into the carbonate form. This implies that a reversible transformation of alkali carbonate to surface carboxylic groups takes place, and indicates that impregnating coals with carbonates would be a reasonable model for studying release of organically bound sodium in coal.

Alkali carbonate has been studied as a catalyst for coal gasification reactions. Yuh and Wolf (1984) impregnated coal samples with Na₂CO₃, NaHCO₃, NaOH, NaNO₃, and NaCl and devolatilized at 1173 K. They showed that each of the sodium salts, except NaCl, transformed to the carbonate form. Their thermogravimetric analysis suggested that at 1173 K NaCl vaporized as sodium chloride. Comparison to results discussed above, which showed sodium and chlorine in coal vaporizing separately, suggests that sodium and chlorine exist separately in the coal matrix. In contrast to NaCl, Yuh and Wolf claimed that not much sodium was lost at 1173 K from chars when sodium was in the carbonate form. They also claimed that "in the presence of a carbon substrate the carbonate is reduced by the substrate at temperatures much lower than those required for the decomposition of sodium carbonate" and that the sodium carbonate was reduced to metallic sodium.

Decomposition of sodium carbonate in the presence of carbon occurs at temperatures below the decomposition temperature in the absence of carbon (Feriks et al. (1981)). Wigmans et al. (1983) wrote the decomposition of the carbonate stoichiometrically as

followed by a reduction of sodium oxide

They claimed that condensed sodium metal in cooler parts of their experimental apparatus supported the reduction reaction. The reduction mechanism in reaction 6.4 is in contrast to that proposed by Hastie et al. (1982), McKee and Chatterji (1978), and Sams and Shadman (1986) who used graphite impregnated with sodium carbonate and observed CO consistent with reaction 6.2. Yuh and Wolf (1984) also found that reaction 6.2 was consistent with reduction of sodium carbonate in graphite, but that the mechanism given by reactions 6.3 and 6.4 was consistent with coal doped with sodium carbonate.

Sams and Shadman (1986) proposed the following mechanism for the reduction of potassium carbonate in graphite:

Reaction 6.5 is consistent with the observations by Wigmans et al. (1983), and Yuh and Wolf (1984) of the formation of surface carboxylic groups from carbonate. Reaction 6.5, 6.6 and 6.8 are consistent with observations for carbonate-coal systems given stoichiometrically by reactions 6.3 and 6.4. Sams and Shadman claimed that reaction 6.6 was negligible in their carbonate-graphite system. Reactions 6.5, 6.7, and 6.8 are consistent with the carbonate-graphite system given stoichiometrically by reaction 6.2. The last reaction, 6.9, represented release of alkali from the carbon surface. Sams and Shadman claimed that reduction was necessary before rapid loss of alkali and cited Shadman et al. (1984) and Sams et al. (1985). The last reaction suggests that vaporization of alkali from the coal matrix would follow first order kinetics.

Talverdian (1984) working with potassium carbonate as a catalyst for gasification of coal chars also claimed that loss of potassium was from the reduced form -CM in contrast to reduction of sodium oxide. Talverdian postulated first order kinetics which fit the data reasonably. Some potassium however, remained in the char and was accounted for by $[\text{K}]_s$ in the following reaction mechanism.

$$\frac{d[K]}{dt} = -a([K] - [K]_s) \quad (6.10)$$

Using a similar system, Sams (1985) showed that alkali vaporized rapidly during reduction of alkali catalyst in graphite. Sams also showed that potassium hydroxide and potassium carbonate behaved similarly during gasification although a slight loss of potassium hydroxide was noted before it was reduced. This was consistent with the work by Yuh and Wolf (1984).

In more recent work Punjak (1988) also found CO release from graphite impregnated with alkali carbonate consistent with reaction 6.2 for both K and Na. Following reduction, Punjak claimed that alkali vaporizes rapidly and the "retention limit" mentioned by Sams (1985) and Talverdian (1982) for the carbon substrate used was a factor of 2.5 lower for sodium than for potassium at 0.0008 mol Na per mol C. Punjak also postulated that reduced alkali vaporizes by reaction 6.9.

Although several steps are involved in the reduction of sodium from coal char, release can be modeled using first order kinetics. Neglecting alkali retention in the char this can be written as:

$$\frac{dC_s}{dt} = -k_s C_s \quad (6.11)$$

The concentration of sodium bound to char was defined by C_s , and k_s was the first order reaction coefficient modeled using an Arrhenius expression. For a constant heating rate, the equation can be written in terms of the temperature, T , only.

$$\frac{dC_s}{dT} \frac{dT}{dt} = -A_s e^{-E_s/RT} C_s \quad (6.12)$$

Defining the constant heating rate dT/dt as ϕ , this equation can be rearranged.

$$\ln \left(\frac{1}{C_s} \left(-\frac{dC_s}{dT} \right) \right) = \ln \left(\frac{A_s}{\phi} \right) - \frac{E_s}{RT} \quad (6.13)$$

Equation (6.13) implies a linear relationship with the inverse of absolute temperature.

In the constant heating rate experiments described by Srinivasachar et al. (1990a), the data were given in absorbance as measured by atomic absorption. Noting that absorbance is proportional to concentration at low values (Beer-Lambert law), their data can be used to

estimate a frequency factor, A_s , and activation energy, E_s , for release of sodium from the organic matrix. Data were normalized so that the area under the absorbance curve was unity. Rate of release was assumed proportional to the concentration measured in the gas phase. The concentration of organically bound sodium was the difference between unity and the integral of the normalized absorbance curve from low temperature to the temperature of interest. These data are given as open circles in Figure 6.6-30. Although the integral of the absorbance curve was determined over the full data range, data presented in Figure 6.6-30 were for points on the curve with a relatively high signal to noise ratio. The linear plot in Figure 6.6-30 supports first order reaction kinetics for release of reduced organically bound sodium from coal char.

Release of organically bound sodium from coal char follows several steps. The reversible transformation of alkali carbonate to surface carboxylic salt groups is among those steps. In a reducing environment, formation of surface alkali oxygen groups occurs. This is followed by reduction of surface carboxylic and phenolic alkali groups to -CM liberating CO in graphite and both CO₂ and CO in coal. The final liberating step, given by reaction 6.9, can be modeled using first order kinetics.

FIGURE 6.6-30. - Arrhenius plot for heating rate experiment by Srinivasachar et al. (1990).

6.6.2.3 Sodium Gas Phase Chemistry

Subsection 6.6.2.2 concluded that reduced sodium in the form of $(\text{-CNa})_{(s)}$ vaporizes as metallic sodium into the pore structure of char particles during coal combustion. Metallic sodium vapor, in the reducing atmosphere inside char, can encounter mineral matter as it diffuses to the char surface. Upon escaping the char, sodium encounters the complex chemistry of the flue gas phase. The form of sodium in the flue gas phase dictates its chemical reactivity, transport properties and condensation characteristics.

Once in the flue gas phase, sodium can be affected by a number of species such as H_2O , O_2 , CO , OH , H , SO_2 , and Cl . Subsection 6.6.1 discussed the behavior of sodium in the presence of these species at equilibrium. Equilibrium calculations showed that sodium hydroxide was the principle form of vapor sodium in the absence of chlorine above 1400 K. When chlorine was present sodium chloride was the principle vapor species, but hydroxide was still significant. Sodium sulfate was not a major vapor species, but it was notable between 1200 and 1500 K in the absence of chlorine. Sodium sulfate was an important condensed phase in the presence and absence of chlorine. Equilibrium calculations were consistent with Boni et al. (1990) who used the SOLGASMIX equilibrium software (Eriksson (1975)).

It is important to note that equilibrium calculations performed in Section 6.6.1 used only pure condensed phases, and the number of condensed phases was limited. Validity of equilibrium calculations applied to a heterogeneous system not at equilibrium should be also questioned. Srinivasachar et al. (1990a) (also discussed in Boni et al. (1990) and presented in Srinivasachar et al. (1989)) performed a kinetic study of sodium in the vapor state. In absence of chlorine and sulfur, they showed that levels of atomic sodium (as released from char) decayed rapidly at 1300 and 1900 K "decreasing to less than 1% of the initial 1 ppm value in less than 20 ms". This time scale is relatively fast for combustion systems with residence times on the order of seconds, and suggests near equilibrium for the gas phase. They listed the following four reactions as important:

At both temperatures sodium hydroxide was the dominant vapor species which was consistent with equilibrium calculations.

In the presence of sulfur, it is not clear if sodium sulfate forms in the vapor at high temperatures (Srinivasachar et al. (1990a)). Equilibrium calculations described in the previous subsection of this report suggested that Na_2SO_4 was not a significant vapor species above 1500 K. Existence of sodium sulfate on boiler tubes could be a result of a gas solid reaction between vapor sulfur and condensed sodium (Steinberg and Schofield (1990)). This postulate is consistent with equilibrium calculations (Subsection 6.6.1) that showed sodium sulfate as an important condensed species below approximately 1200 K.

With chlorine introduced to their calculations, Srinivasachar et al. (1990a) calculated that initial concentrations for Na and Cl of 1 ppm "declined by several orders of magnitude within 3 to 5 ms subsequent to onset of oxidizing conditions at 1500 K". Sodium hydroxide was the dominant form of sodium for this system and they claimed that the calculated "equilibrium levels of chloride and the hydroxide were in good agreement with the kinetically determined levels". At higher levels of chlorine, the chloride form of sodium dominated the vapor species. They showed that kinetics in the gas phase was relatively fast and equilibrium (or near equilibrium) was attained quickly with respect to time scales in combustion systems. This suggests that equilibrium calculations, at least for the gas phase, can give insight into alkali behavior in post flame combustion systems.

6.6.2.4 Sodium Interaction with Silicates

6.6.2.4.1 Past Work

In addition to gas phase reactions discussed in the previous section, sodium also participates in gas solid reactions with silicates (Wibberly and Wall (1982a,b)). Huffman et al. (1990) claimed that "sodium reacts strongly with clay (mainly kaolinite in lignite) and quartz, both within the burning coal particle and in the vapor phase". This was consistent with CCSEM information (Subsection 6.5.6) which showed reaction products of sodium with both kaolinite and quartz.

Reaction of sodium with silicates can be referred to as capture since sodium is not expected to vaporize from silica melts (Boni et al. (1987)). Capture of sodium by silicates might be considered detrimental. It has been found that viscosity of silicate glasses decreases (stickiness increases) with increasing alkali content (Paul (1990)). Lower viscosity results in ash more susceptible to sticking on boiler tubes and other surfaces during impaction (Srinivasachar et al. (1990b), Boow (1972)).

Combustion systems can also take advantage of alkali capture by silicates. Removal of vapor sodium species in the gas phase or through packed beds is a technique which has received some study (Scandrett and Clift (1984), Bachovchin (1986), Wendt et al. (1987), Punjak (1989), Uberoi (1990)).

Past work has discussed the influence of silicates on the fate of sodium during pulverized coal combustion (Neville and Sarofim (1985)). Lindner et al. (1988, 1990) and Lindner (1988) studied reaction of sodium with included silica (silica inside the char particle)

and kaolinite in a drop tube furnace. They used a cleaned low-ash coal that was doped with a sodium source and/or a silicate.

Lindner et al. (1988, 1990) showed that sodium, added as either sodium acetate or sodium chloride, can react with included silicates. Conclusions drawn from experiments using NaCl are not expected to be valid when extrapolated to coal systems with organically bound sodium. Yuh and Wolf (1984) showed that NaCl added to chars did not behave as organically bound sodium, and Srinivasachar et al. (1990a) showed that NaCl vaporizes at temperatures far lower than organically bound sodium. There is evidence that sodium carbonate added to chars decomposes and behaves as organically bound sodium, and it is expected that sodium acetate added to coal would be more representative of organically bound sodium than NaCl.

Using NaCl and silica, Lindner et al. (1988, 1990) concluded that reaction between sodium and silica was negligible after char burnout was complete and attributed these results to a lowering of available silica surface area due to agglomeration and coagulation. Using NaCl and kaolinite instead of silica, capture was higher which is consistent with results of Punjak et al. (1989) and Uberoi et al. (1990). Punjak et al. and Uberoi et al. performed experiments with sodium chloride vapor and kaolinite pellets suggested a possible reaction mechanism as the following:

Punjak et al., Uberoi et al., and Bachovchin et al. (1986) also noted that water was necessary for capture of NaCl by silicates. Bachovchin et al. claimed that water was not consumed, but sodium concentrations on the order of ppm would not have a marked effect on moisture concentrations generally in the per cent range. Lindner et al. (1988, 1990) also claimed that sodium silicate formation was significantly higher when sodium acetate was used instead of sodium chloride (sulfur depressed sodium silicate formation only slightly). This suggests that the mechanism of capture of sodium chloride by kaolinite might proceed as follows:

This mechanism sums to the overall reaction proposed by Punjak et al. and Uberoi et al. (6.18).

Lindner and Wall (1988) burned a synthetic coal in a drop tube furnace to study the reactions and reaction mechanisms of sodium with inherent silicates during coal combustion. After acid leaching a Loy Yang coal to remove ion exchangeable metals sodium was added as a solution of NaCl or sodium acetate. The coal contained either inherent silica or kaolin

and was fired at temperatures of 1000, 1200, and 1400°C. Their results showed that formation of sodium silicate was greater in the absence of chlorine, and was also higher for kaolinite than for silica. To investigate effects of sodium release, two coals were burned together. One coal contained only inherent silica, and the other either NaCl or sodium acetate. Differences in extent of reaction between 1000 and 1200°C ($E_{1200-1000}$) were greater for the experiments with separated sodium and silica than in experiments where they existed together. From this they concluded that at 1200 and 1400°C the sodium was completely released prior to onset of sodium silicate formation, however at 1100°C both NaCl and sodium acetate had not completely vaporized prior to silicate formation. A possible explanation suggested by Lindner and Wall (1990) is that there is "little reaction of sodium with silica as it evaporates". This implies that although the sodium in the separated experiments did not completely vaporize at 1000°C, it did completely vaporize in the experiments where they existed together, or that some other mechanism allowed for less of a difference in $E_{1200-1000}$ for the experiments where sodium and silica existed together. Also, no explanation was provided for a larger difference in $E_{1400-1200}$ which was of comparable magnitude to $E_{1200-1000}$ for the separated experiments compared to experiments where the sodium and silica coexisted. Unfortunately direct comparisons of the extent of sodium capture for separated and coexisting sodium and silica could not be made since the concentrations of each specie was not identical across the experiments. It was difficult to conclude from these experiments if sodium reacts with inherent silicates as it evaporates. It is clear that sodium which is released from the coal can diffuse into char particles and react with included silicates. These experiments also showed that alkali capture was greater with kaolinite than silica.

6.6.2.4.2. Present Work

Experiments involving pulverized Loy Yang 2301 coal doped with extraneous kaolinite additive were performed in this study to investigate sodium/silicate interactions. Loy Yang was chosen since it had a high sodium to silicate ratio and low silicates overall. Comparisons of doped Loy Yang burns (41 and 42) were made with unadulterated Loy Yang (burn 39).

Loy Yang was used in burn 39 (Subsection 6.5.2.4) at two feed rates with peak temperatures of approximately 1260 and 1340°C. Three impactor samples were acquired: (A) corresponded to the lower peak temperature, and (B) and (C) to the higher peak temperature. Figures 6.5-56 and 6.5-57 showed significant enrichment of Na in the small sizes in fraction oxide versus impactor stage plots for both temperatures.

Figures 6.6-31 and 6.6-32 show the cumulative fraction of Na₂O and K₂O as a function of particle size for burn 39. The 50% cutoff diameter, d_{p50} , was chosen as representative of an impactor stage's size class. A significant fraction (approximately 75%) of sodium was found in a size range less than 0.65 μm in both high and low temperature burns. Differences in peak temperatures did not significantly affect the sodium behavior. This suggested that a temperature dependent sodium reaction with silicates was not significant. This was a consequence of insufficient silicate matter in Loy Yang.

FIGURE 6.6-31. - Cumulative fraction for sodium burn 39.

FIGURE 6.6-32. - Cumulative fraction for potassium burn 39.

Although the original amount of potassium in the parent coal was very low, a significant fraction of potassium in the fly ash was in the smallest sizes (Figure 6.6-32). In contrast to sodium results, a greater fraction of potassium was in the smallest sizes for samples taken at the higher temperature. The temperature dependence of potassium would be consistent with displacement of potassium originally bound in silicate such as illite. Higher temperatures would result in faster reaction of sodium with potassium-containing silicates. The result would be faster displacement of potassium by sodium at higher temperatures. The original form of potassium in Loy Yang, however was unknown. The apparent contradiction of no observed temperature dependence of the sodium size distribution is explained by a high sodium-to-silicate ratio.

Burns 41 and 42 used Loy Yang doped with 94g kaolinite per kg additive-free coal such that the sodium-to-silicate ratio was close to Beulah Lignite. Burgess Pigment Company reported that the kaolinite had a mass mean diameter of $0.5 \mu\text{m}$ and density 2.63 g/cm^3 (aerodynamic size of approximately $0.8 \mu\text{m}$). Subsection 6.4 showed the original ash analysis and calculated ash analysis for the doped coal using the kaolinite analysis supplied by Burgess.

Only one impactor sample was acquired in burn 41 because coal stopped feeding due to bridging in the feeder. The temperature profile for burn 41 was shown in Figure 6.5-70 (Subsection 6.5.3.1) and had a peak of roughly 1010°C which was significantly lower than both peak temperatures realized in burn 39. Figure 6.5-72 showed the fraction oxide plot for burn 41. Comparison to results from burn 39 showed a significant influence of kaolinite additive. CCSEM gave evidence of nepheline formation. Sodium, however still dominated the after-filter.

Figures 6.6-33 and 6.6-34 show the cumulative fraction plots for sodium and potassium as oxides for burn 41. The fraction of sodium in a size range less than $0.65 \mu\text{m}$ dropped from approximately 75% in burn 39 to roughly 12% for the doped run. The additive significantly changed the sodium distribution but it is still not clear if the mechanism was increased chemical reaction between sodium and silicates, or if the additive served only as additional sites for condensation. Both mechanisms would shift sodium mass to the larger size classes.

Doped Loy Yang contained approximately 0.052g Na per g silicates (Na/Si) where silicates was SiO_2 in the parent coal plus 94g kaolinite per kg raw coal. The ratio Na/Si for Beulah Lignite was approximately 0.065 where silicates was a sum of quartz, kaolinite, illite, montmorillonite, mixed and miscellaneous silicates. Comparing these two ratios (Na/Si) would suggest that doped Loy Yang would exhibit a lower fraction of sodium in a size range less than $0.65 \mu\text{m}$ due to capture. Figure 6.6-35 shows the sodium cumulative fraction plot for Beulah Lignite (Subsection 6.5.2.3 burn 38). Sample A had an approximate peak temperature of 1285°C and for samples B and C it was 1132°C . For Beulah Lignite, the average fraction of sodium less than $0.65 \mu\text{m}$ was roughly 9.5% compared to approximately 12% for doped Loy Yang. Therefore, it can be concluded that the additive did not capture as much as expected.

FIGURE 6.6-33. - Cumulative fraction for sodium burn 41.

FIGURE 6.6-34. - Cumulative fraction for potassium burn 41.

FIGURE 6.6-35. - Cumulative fraction of sodium for burn 38.

Silicate matter in doped Loy Yang was dominated by extraneous additive as compared to Beulah Lignite which is known to have a significant fraction of its silicate matter existing inherently. Since capture in the doped Loy Yang burn was lower than for Beulah Lignite, this implied that capture of sodium by extraneous silicate matter by reaction and/or condensation was less efficient than capture by inherent silicate matter. The difference in capture, however might be explained by lower temperatures realized in burn 41.

To test the relative importance of condensation and reaction, samples in Burn 42 were subjected to a solubility analysis. Burn 42 also used doped Loy Yang (Subsection 6.5.3.1). Figure 6.5-71 showed temperature profiles corresponding to two samples collected. Two different feed rates were used in an attempt obtain two different peak temperatures. The different feed rates however, succeeded primarily in changing the two profiles and changed the peak temperature only slightly. Sample A and B had approximate peak temperatures of 1360°C and 1340°C respectively.

A solubility analysis was applied to impactor samples from burn 42. Collected samples were cut into halves. One half, dissolved in a combination of HCl, HNO₃, and HF acids, was assumed to represent total sodium content, and the second half was dissolved in deionized (DI) water and was assumed representative of condensed sodium. The difference represented chemically reacted or fixed sodium.

Literature suggests that only a few sodium silicates are water soluble. CCSEM analysis (Subsection 6.5.6) and Punjak et al. (1989) showed evidence that the reaction product of sodium with kaolinite is nepheline (Na₂O·Al₂O₃·2SiO₂). Nepheline is insoluble

in cold water and decomposes in hot water (CRC (1981)). DI samples in this investigation were never subjected to temperatures above 40°C. Albite and jadite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) were also reported as insoluble. Equilibrium calculations (Subsection 6.5.1) suggested a reaction product of sodium with quartz was $\text{Na}_2\text{Si}_2\text{O}_5$. This was reported as soluble, however the amount of quartz in Loy Yang was low. Capture by quartz is also expected to be low due to its low specific surface area. Bachovchin et al. (1986) mentioned the formation of a sodium silicate glass outer layer on emathlite ($\sim \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$) pellets exposed to sodium chloride vapor at 800°C. In contrast, examination of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) pellets exposed to NaCl at 800°C by energy dispersive x-ray analysis gave no indication that this water soluble complex formed (Punjak (1988), and Uberoi (1990)). Therefore, formation of a water soluble silicate glass in kaolinite or with quartz was not expected to account for a significant fraction of sodium capture, and the DI water soluble sodium was expected to represent condensed sodium.

Fraction oxide plots for burn 42 are shown in Figures 6.5-73 and 6.5-74 (Subsection 6.5) for acid dissolved samples. The two samples, A and B, were very similar and also compared well with the fraction oxide plot for burn 41 in Figure 6.5-72. Burn 41 however showed a greater enrichment of sodium in the smallest sizes. This was consistent with a sodium reaction with kaolinite additive since burn 41 had lower temperatures (and thus slower capture). The fraction of sodium in each size class and the total filter was also slightly higher in burn 41 than either samples of burn 42. The reason for this difference was not apparent. Plots of sodium cumulative fraction for burn 42 (Figure 6.6-36) were, however very similar to the same plot for the lower temperature burn 41 (Figure 6.6-33).

The potassium distribution for burn 42 (Figure 6.6-37) shifted to the largest sizes compared to the analogous plot for burn 41 (Figure 6.6-34). This could be due to enhanced capture of potassium by additive at the relatively higher temperatures of burn 42.

Results of the solubility analysis are given in Figures 6.6-38 through 6.6-43. Results were given as the concentration of species in flue gas in mg per sm^3 versus impactor plate. The lower portion of the stacked bar represents captured matter determined from water soluble material subtracted from the acid dissolved sample. Error in this number was estimated at 5 to 7.5%. The upper portion of the stacked bar was determined from water solubility data alone and is indicative of condensed material. Experimental error could explain negative values calculated for captured material.

Examination of silicon solubility results (Figures 6.6-38 and 6.6-39) indicated that only a small fraction of silicon was water soluble. This could be attributed to small amounts of water soluble silicon containing minerals present. A small amount of water soluble Si was noted by Bachovchin et al. (1986) for samples of unreacted emathlite. It should also be noted that it was difficult to measure small concentrations of silicon (less than ~ 50 ppm in the analysis solution). Plate 1 samples were near 30 ppm and all others were less than 11 ppm with most near 1 ppm. Although solubility data in this study does show some water soluble silicon in the largest size class, results for stages 2 through the after-filter were inconclusive due to analysis difficulties. It is not expected that the water soluble silicon was associated with the formation of a water soluble sodium silicate.

FIGURE 6.6-36. - Cumulative fraction for sodium burn 42.

FIGURE 6.6-37. - Cumulative fraction for potassium burn 42.

FIGURE 6.6-38. - Burn 42 sample A silicon.

FIGURE 6.6-39. - Burn 42 sample B silicon.

FIGURE 6.6-40. - Burn 42 sample A sodium.

FIGURE 6.6-41. - Burn 42 sample B sodium.

FIGURE 6.6-42. - Burn 42 sample A potassium.

FIGURE 6-6-43. - Burn 42 sample B potassium.

Figures 6.6-40 and 6.6-41 show solubility results for sodium. In contrast to silicon, a large fraction of sodium was water soluble in all size classes. In fact sodium in the smallest sizes (plate 8 and after-filter) was almost entirely water soluble suggesting it was primarily condensed. The large fraction of water soluble sodium in all sizes indicated that capture of vapor sodium by extraneous kaolinite was governed to a large extent by condensation. Chemical reaction leading to fixed sodium was also important but to a lesser extent than was implied by acid soluble data alone. These results suggest that kaolinite additive acted as reaction substrate and condensation site for vapor alkali in nearly equal proportions.

Results shown in Figures 6.6-42 and 6.6-43 show that potassium on plate 8 and the after-filter was also primarily water soluble. Comparison to sodium showed a larger fraction of potassium to be fixed in the larger size classes.

The lower sodium-to-silicon ratio (Na/Si) for Loy Yang doped with kaolinite suggested that capture would be higher than for Beulah Lignite. This comparison can be made for all the coals. As was mentioned previously, quartz is not expected to be as efficient at capturing sodium as other silicates which contain aluminum. Including quartz in the determination of Si for the Na/Si ratio would imply a greater ability for sodium capture than might be expected. Using only aluminosilicates in the calculation of Si content might provide a more accurate determination of relative capture ability. Further, only acid soluble sodium should be used in the Na/AlSi ratio since this would represent sodium that could easily vaporize.

The solubility analysis showed that the fraction of sodium on impactor plate 8 and the after-filter (f_{gA} , less than $0.65 \mu\text{m}$) was almost entirely water soluble. This suggests that the fraction of sodium in this size class was indicative of condensed (not captured) sodium. Figure 6.6-44 shows a plot of f_{gA} for sodium versus Na/AlSi . The open circles are for undoped parent coals (burns 13 through 35). Filled circles are for doped Loy Yang in which the silicate mass was dominated by kaolinite additive (burns 41 and 42). Filled squares are for Kentucky No. 11 doped with sodium acetate (burns 43 and 44). The line is a linear regression to open circles. Figure 6.6-44 suggests that the fraction of sodium captured by silicates depends on both the amount of sodium and silicates present in coal.

Comparison of f_{gA} for doped Loy Yang to the parent coals (filled circles compared to the open circles) suggested that extraneous kaolinite additive did not capture as efficiently as silicates in the raw coals. All three points for doped Kentucky No. 11 (Subsection 6.5.3.2) lie below the line suggesting more efficient sodium capture. Although these data are close enough to be considered inside the scatter, one explanation for these points being lower than for the raw coals is related to the original form of sodium in the doped case. Sodium in the doped Kentucky No. 11 burns was added as extraneous sodium acetate and was expected to vaporize very easily. This suggested, but was not conclusive evidence, that vaporization (or release) of bound sodium is an important step that could limit capture of sodium by silicates. The higher temperatures and hence faster Na-AlSi reaction rates experienced by included silicates (Kentucky 11) versus those experienced by excluded silicates (Loy Yang) might also have contributed to the observed differences.

FIGURE 6.6-44. - Sodium f_{gA} versus Na/AlSi.

6.6.2.5 Sodium Condensation

Sodium can vaporize and be released into the bulk flue gas phase. Sodium that is not captured by silicates in the hot post flame region of a combustor is transported with the flue gas to cooler zones of combustion systems. Reaction rates between sodium and silicates slow significantly in the cooler sections and condensation of sodium species becomes the dominant mechanism governing sodium behavior.

Equilibrium calculations of Subsection 6.6.1 suggested that Na_2SO_4 was an important condensed phase below 1200 K. In high chlorine low sulfur systems like Loy Yang 2301, NaCl can also be an important condensed sodium species below 1100 K.

In the continuum regime (Knudsen number < 1) the rate of heterogeneous condensation is expected to be proportional to particle size, d_p (Friedlander (1977), Hinds (1982)).

$$F = \frac{2\pi d_p D(p - p_{eq})}{RT} \quad (6.21)$$

F is the molar rate of condensation, the diffusivity is D , and the vapor pressure of alkali in the vapor phase and at the particle surface is p and p_{eq} respectively. Multiplying by the

molecular weight of the condensing species and dividing by the total mass of the particle ($M = \pi/6 \rho_p d_p^3$) yields:

$$\frac{d(m_i/M)}{dt} = \frac{12D(p - p_{eq})}{d_p^2 \rho_p RT} \quad (6.22)$$

where the contribution to the total particle mass by the condensing species was assumed to have a negligible affect. If it is assumed that the particle size change due to condensation is negligible and integrate from time $t = 0$ to t_1 an equation relating the fraction of condensed species to particle size can be derived.

$$\frac{m_i}{M} = \frac{1}{d_p^2 \rho_p R} \int_0^{t_1} \frac{D(p - p_{eq})}{T} dt \quad (6.23)$$

This suggests that the fraction of condensing species m_i/M in the aerosol would be linear when plotted against $1/d_p^2$. The slope would be related to the driving force for condensation ($p - p_{eq}$) and residence time t_1 . The diffusivity divided by temperature in the integral is expected to be a mild function of temperature ($\sim T^{1/2}$). Residence time in the combustor is also a function of temperature. Lower temperatures would partially offset an increase in residence time. This suggests that the driving force for condensation takes a larger role in the kernel, and thus the slope, than might be expected on first inspection.

Figure 6.6-45 shows plots of the fraction of sodium (as oxide) versus $1/d_p^2$ for impactor samples of Beulah Lignite fly ash from burns 13, 14 and 38. Impactor 50% cutoff diameters were assumed as representative of a size cut. Lines shown are linear least squares fits to the last three points (impactor stages 6, 7, and 8) where condensation was expected to dominate (in contrast to capture). The after-filter was not included in the plot for a number of reasons: choosing a representative size was difficult, nucleated particles were expected to be important in this size class, and condensation was not expected to follow continuum mechanics.

Plots in Figure 6.6-45 showed that as the peak temperature increased, the slope of the fraction of sodium in ash versus $1/d_p^2$ decreased. As was mentioned above, higher temperatures had shorter residence times which was at least partially offset by a larger kernel. Lower slopes at higher temperatures then suggested a smaller driving force. This was consistent with capture of sodium by chemical reaction since capture would be faster at higher temperatures. This would leave less sodium in the vapor that could participate in condensation at lower temperatures.

FIGURE 6.6-45. - m_{Na}/M versus $1/d_p^2$ for Beulah Lignite.

6.6.2.6 Sodium Behavior Summary

A brief summary of conclusions about sodium behavior is included in this section. The summary included observations made during this study and those of other investigators.

- The mode of occurrence affects sodium behavior. Organically bound sodium and sodium existing as halides are expected to account for sodium that reaches the gas phase. Sodium originally in clays is not expected to vaporize.
- Evidence of sodium vaporization during coal combustion was shown in the marked enrichment of alkali in the small sizes for coals like Beulah Lignite and Loy Yang. Sodium in Beulah Lignite (8400 ppm Na, 95 ppm Cl) and Loy Yang (5100 ppm Na, 7500 ppm Cl) does not vaporize as sodium chloride. Sodium and chlorine are liberated from low-rank coal separately and at markedly different temperatures. Sodium salts in coal Na_2CO_3 , $NaHCO_3$, $NaOH$, and $NaNO_3$ each transformed to the carbonate form. $NaCl$ in coal devolatilized at 1173 K indicating that $NaCl$ vaporized as sodium chloride. These results suggest that sodium and chlorine exist separately in the coal matrix.
- A reversible transformation of alkali carbonate to surface carboxylic groups can take place which indicates that impregnating coals with carbonates would be a reasonable model for studying release of organically bound sodium in coal. In the presence of a carbon substrate, carbonate is reduced by the substrate at temperatures lower than

those required for decomposition of sodium carbonate and is reduced to metallic sodium. Reduction of one mole of carbonate in graphite produces three moles of CO. Reduction of one mole of carbonate in coal produces one mole each of CO and CO₂. Sodium vaporization ($\text{-CNa} \rightarrow \text{Na}_{(g)}$) follows first order kinetics.

- The time scale for reaction of sodium in the gas phase (0.003 to 0.02s) is fast when compared to combustion time scales (1s). This suggests that near-equilibrium is a reasonable approximation for the gas phase. Sodium hydroxide and sodium chloride are the two dominant gas phase species. The relative levels of each species depend on concentrations of chlorine and moisture.

- Equilibrium suggested that sodium sulfate was not a significant vapor species above 1500 K, but was a significant condensed species below 1200 K. The existence of sodium sulfate on boiler tubes could be the result of a gas-solid reaction between vapor sulfur and condensed sodium.

- Results of CCSEM analysis showed evidence that sodium chemically reacted with both kaolinite and quartz. Sodium reaction with silicates begins prior to complete release of sodium to the bulk vapor phase. It is unclear if reduced metallic vapor sodium reacts with included silicates as it diffuses to the char surface. Sodium in the bulk vapor phase can diffuse into the char and react with included silicates. Reaction between sodium and included silica is negligible after char burnout is complete. This suggests a lowering of available silica surface area due to coalescence. Kaolinite is more efficient at sodium capture than silica.

- Capture of sodium by silicates from $\text{NaCl}_{(v)}$ required the presence of moisture. A measurable amount of water was not consumed and the sodium silicate reaction product did not contain chlorine. Sodium silicate formation was significantly higher in the absence of chlorine (sulfur depressed sodium silicate formation only slightly). These results suggest that the first step in the mechanism of capture of sodium chloride by kaolinite is equilibrium of NaCl with NaOH. The second step is reaction of sodium hydroxide with the silicate.

- For Loy Yang, the fraction of sodium in a size range less than 0.65 μm dropped from approximately 75 to 12% when 94g of kaolinite per kg coal was added. The additive significantly changed the sodium distribution. Capture by extraneous kaolinite additive in doped Loy Yang burns was lower than for the parent coals in the base suite. This implied that capture of sodium by extraneous silicate matter by reaction and/or condensation was less efficient than capture by inherent silicate matter. Extraneous kaolinite additive acted as a reaction substrate and condensation media for vapor alkali in nearly equal proportions. Doped Loy Yang burns showed that the fraction of sodium on impactor plate 8 and the after-filter (f_{gA} , $< 0.65 \mu\text{m}$) was almost entirely water soluble.

Capture of sodium for Kentucky No. 11 doped with extraneous sodium acetate was more efficient than for coals in the base suite. Extraneous sodium acetate was expected to vaporize more readily than organically bound sodium. This suggested that vaporization of bound sodium from char is an important step that could limit capture of sodium by silicates.

Linear plots of the fraction of sodium in ash versus $1/d_p^2$ showed condensation of sodium occurs on existing fly ash particles in cooler regions of combustion systems. Decreasing slope with increasing temperatures suggested lower vapor sodium concentrations with increasing temperature. This was consistent with increasing capture of sodium by chemical reaction with increasing temperatures.

6.6.3 Sodium/Potassium Interactions

In contrast to organically bound sodium which readily vaporizes, potassium commonly exists in aluminosilicate clays and is naturally irvolatile. Initial studies attributed sodium chloride to releasing potassium from silicate minerals (Raask (1968, 1985)). Other studies blamed release of mineral potassium on chlorine (Gibb and Angus (1983)).

Vaporization of potassium depends on its initial form in coal. Organically bound potassium is expected to vaporize easily, while release of mineral potassium is expected to depend on other species present. Size-segregated fly ash samples collected in this study showed evidence of potassium vaporization in a laboratory scale combustor. Bench scale experiments were performed with potassium aluminosilicates to isolate potassium release mechanisms.

6.6.3.1 Mode of Occurrence of Potassium

Alkali behavior during pulverized coal combustion is dictated by its mode of occurrence and its interactions with other minerals present. Unlike sodium, potassium is primarily bound in mineral matter as potassium aluminosilicates (Bryers (1988)). Illite ($KAl_2(AlSi_3O_{10})(OH)_2$) is a common potassium rich clay in coal (Raask (1985)) and was a major mineral constituent in bituminous coals used in this study (Sections 3 and 4).

Determining the relative mode of occurrence of potassium in coals used in this study was difficult. An estimate of the amount of mineral bound potassium can be made from acid soluble K subtracted from ash K (Table 6.6-4). This estimate suggests that roughly 30 % of the potassium in Kentucky No. 11 was bound in mineral matter. An estimate can be made from elemental mineral compositions (Section 4). Using K in quartz, illite, and miscellaneous silicates, and assuming each mineral mass is half oxygen (O was not reported and this represents a reasonable upper limit), a value of 4753 ppm mineral K is calculated for Kentucky No. 11. This is higher than the ash value suggesting all the K is bound in the mineral matter. It is suspected that K exists primarily in mineral matter for the bituminous coals even though some was listed as acid soluble. It is possible that leaching from clays is the source of acid soluble potassium.

TABLE 6.6-4. - K, Na, and Cl for base suite of coals

Coal	Acid Sol K (ppm) ¹	Ash K (ppm) ²	Ash - Acid Sol (ppm)	Acid Sol Sodium (ppm) ¹	Chlorine (ppm) ³
Beulah Lignite	160	241	81	7375	95 ⁴
Eagle Butte	95	80	-15	820	NA
Illinois No. 6	2380	1810	-877	2258	911 ⁴ 1200 ⁵
Upper Freeport	2350	5978	3628	360	NA
Kentucky No. 9	2550	3093	543	525	700 ⁵
Kentucky No. 11	2919	4211	1292	383	300 ⁵
Loy Yang 2301	N	< 1000	NA	5100	7550
¹ Average of two numbers from Table 3-14, Section 3. ² Elemental K from as-received K ₂ O (Table 3-15, Section 3). ³ Dr. J. Helble, PSI Inc. personal communication for all values except Loy Yang 2301. ⁴ Atomic absorbance on 65 to 73 μ m fraction. ⁵ Bomb analysis.					

Spiro et al. (1986) examined the form of K in several coals using high resolution x-ray absorption near-edge structure (XANES) measurements. For bituminous coals K was found to be bound in the layered clay illite. Potassium appeared in a non-crystalline form for sub-bituminous and lignite coals. For low-rank coals, including Beulah Lignite, K XANES spectra did not resemble spectra of organic potassium salts (acetate, benzoate, and oxalate) nor spectra of phthalimide or t-butoxide. This suggests that K in these coals did not exist bound to the organic matrix. Leaching with HCl changed the spectra intensity, but did not alter the XANES spectrum. Leaching of illite-containing bituminous coals with HCl/HF gave a spectra similar to the low-rank coals. Spiro et al. speculated that the K might be absorbed on a range of surfaces including clays and the organic matrix. This suggests that K in low-rank coals would vaporize easier than in bituminous and high-rank coals.

6.6.3.2 Potassium Release in a Laboratory Combustor

Eagle Butte and Beulah Lignite showed potassium enrichment of the smaller size classes in fraction oxide plots (Subsection 6.5), and Loy Yang showed a significant fraction of potassium in the small sizes (Figure 6.6-32). This evidence suggests vaporization of K during combustion of these low-rank coals. Fraction oxide plots and cumulative fraction plots for bituminous coals did not show evidence of significant potassium vaporization. This is consistent with the original form of potassium discussed above.

Potassium is expected to react with silicates in a manner similar to sodium. Potassium reactions with kaolinite and illite have been observed in coal doped with potassium carbonate (Kühn and Plogmann (1983)). For sodium, a plot of the fraction of sampled alkali on impactor plate 8 plus the after-filter (f_{8A}) as a function of acid soluble alkali divided by aluminosilicates (Na/AlSi) gave a positive correlation (Figure 6.6-44). A similar plot for potassium (Figure 6.6-46) does not show a positive correlation. In fact, with the exception of data for Loy Yang 2301, a negative correlation is suggested. Data for Loy Yang 2301 was estimated by assuming a molar equivalent of kaolinite for Al_2O_3 , and $<0.01\%$ K on a dry basis was 0.005% . A possible explanation is that acid soluble K is leached from mineral matter and does not represent readily vaporized K. Another explanation is that vaporization of mineral K is enhanced by other species such as NaCl.

FIGURE 6.6-46. - Potassium f_{8A} versus K/AlSi .

Bomb combustion experiments, a significantly different mode of combustion, suggested that NaCl contributed to release of nonvolatile mineral K (Raask (1985), Raask (1968)). Gibb and Angus (1983) performed bomb coal combustion experiments with NaCl, $\text{NaOOCH}_2\text{CH}_3$, and NH_4Cl additives, and concluded that the major contribution to K release was attributable to Cl.

Experiments in this study suggested a correlation between the fraction of vaporized K and Na indicated by f_{8A} (Figure 6.6-47). A similar plot can be made using vaporized alkali data presented by Gibb and Angus (1983). The correlation of K f_{8A} versus Na f_{8A} together with the lack of a correlation of K f_{8A} with K/AlSi suggests that Na might be involved in the displacement of K from mineral matter.

A plot of K f_{8A} as a function of coal Cl content is shown in Figure 6.6-48. The low-rank coals suggest a positive correlation of K vaporization and Cl content. This is consistent with equilibrium calculations (Subsection 6.6.1). Potassium vaporization for Beulah Lignite and Loy Yang, however could also be linked to high sodium content, and the original form of potassium. The bituminous coals suggest no correlation between K vaporization and Cl content. Of the three bituminous coals shown, Illinois No. 6 has the highest content of Cl and acid soluble Na. Kentucky No. 11 has the lowest of both species yet the K f_{8A} is comparable.

FIGURE 6.6-47. - K versus Na in small sizes.

FIGURE 6.6-48. - Potassium f_{gA} versus chlorine content. Filled squares are for Kentucky No. 11 with NaAc.

To test the hypothesis that sodium can displace potassium bound in mineral matter, burns 43 and 44 used Kentucky No. 11 with extraneous sodium acetate additive (NaAc). Sodium in NaAc was expected to readily vaporize and participate in sodium-silicate interactions. Kentucky No. 11 was chosen due to its high illite content, and low Na and Cl content. Illite is an aluminosilicate with a relatively high occurrence of potassium. Experiments with clean Kentucky No. 11 showed a low f_{gA} for both potassium and sodium.

Burns 43 and 44 used doped coal: Kentucky No. 11 with 98.86g sodium acetate trihydrate per kg additive-free coal. This gave a ratio of sodium-to-silicate in the doped coal that was similar to that in Beulah Lignite. NaAc granules were broken up by hand and screened into the coal. The mixture was blended until homogenous to the eye then screened again to break up any undetected agglomerates. NaAc particles were in general larger than coal particles which ensured that the sodium would be external to char particles during combustion.

During burn 43, two full impactor samples were acquired corresponding to the two temperature profiles shown previously in Figure 6.5-75. Sample A had a peak temperature of approximately 1455°C and for sample B it was 1290°C. The temperature profile for the single sample from burn 44 was shown in Figure 6.5-76. Its peak temperature was approximately 1258°C. As a comparison, three full impactor samples were acquired during burn 37 which used clean Kentucky No. 11. Temperature profiles for burn 37 were shown in Figure 6.5-50. Sample A had a peak temperature of approximately 1261°C and samples B and C had a peak temperature of approximately 1105°C.

Fraction oxide plots for burns 43 and 44 (Figures 6.5-77 through 6.5-79) all showed sodium enrichment in the small sizes to some extent. Burn 37 (Figures 6.5-51 and 6.5-52) showed no alkali enrichment in the small sizes which reflected the low sodium content of the clean Kentucky No. 11 coal.

Table 6.6-5 lists the $K f_{8A}$ for each impactor sample from burns 37, 43 and 44. The $K f_{8A}$ for burn 37 was approximately 0.1%, and for burns 43 and 44 it ranged from 0.5 to 2%. Figure 6.6-49 shows the $K f_{8A}$ for doped burns (43 and 44) compared to undoped burns of Kentucky No. 11 (27, 28, and 37). Comparison showed a significant increase in the fraction of potassium in the small size ranges for the doped burns (Figure 6.6-49). This showed that the addition of extraneous sodium can aid in the release of potassium from aluminosilicates.

The fraction of K in the small sizes for burns 43 and 44, however was lower than that for the Beulah Lignite (burn 38) which ranged from approximately 3 to 6%. This could be due to the original form of potassium in Beulah Lignite which was expected to vaporize more easily.

TABLE 6.6-5. - Potassium f_{8A} for Kentucky No. 11

Sample	Coal	Peak Temp (°C)	Fraction of K on 8 + AF
43 acid A	Kent No. 11 + NaAc	1455	0.017
43 acid B	Kent No. 11 + NaAc	1290	0.016
44 acid A	Kent No. 11 + NaAc	1258	0.005
37 A	Kent No. 11	1261	0.001
37 B	Kent No. 11	1105	0.000 8
37 C	Kent No. 11	1105	0.000 9
38 A	Beulah Lignite	1285	0.028
38 B	Beulah Lignite	1132	0.063
38 C	Beulah Lignite	1132	0.043

6.6.3.3 Potassium Release in a Bench Scale Reactor

Bench scale experiments with potassium aluminosilicates were conducted in an effort to clarify possible mechanisms of K release from mineral matter. The relative importance of the presence of Na and K was also tested. Two potassium rich silicates were used in this study: naturally occurring illite, and kaolinite calcined with $KOH_{(aq)}$. An illite standard from Fithian, Illinois was acquired from the Geology Department at the University of Arizona. An artificial potassium rich clay was produced by impregnating a sample of ground

FIGURE 6.6-49. - Potassium f_{8A} for Kentucky No. 11.

kaolinite with $\text{KOH}_{(aq)}$ and heating. Both silicates were ground in an agate mortar and compressed into pellets prior to experimentation.

6.6.3.3.1 Experiments with Kaolinite Impregnated with Potassium

An artificial potassium silicate was produced with clean kaolinite and KOH . The procedure included placing $1.66844 \pm 0.00005\text{g}$ kaolinite and $0.27505 \pm 0.00005\text{g}$ KOH with a few drops of deionized water into a quartz bowl. The mixture was heated to 350 to 400 K for 42 min then to 1070 K for 340 min with an N_2 purge. The product, KaoK, was removed and ground to a fine powder in an agate mortar before compressing into a pellet.

Atomic absorbance (AA) analysis for KaoK powder and a KaoK pellet which was heated to 1070 K for approximately 26 hr showed no change in the $\text{K}/(\text{Al}+\text{Si})$ ratio. As-received illite and an illite pellet which heated to 1270 K also showed no change in the ratio of $\text{K}/(\text{Al}+\text{Si})$. This was confirmed with additional samples of illite heated to 1070 K for extended periods (13 to 141 hours) and was consistent with the results reported by Srinivasachar et al. (1990b) for illite heated to 1500 K.

Pellets of potassium silicate were prepared by placing 10 to 20 mg of ground sample into a stainless steel die 8 mm in diameter. The sample was pressed for 1 min at 26700 N (6000 lb_f).

Although Na and Cl vaporize separately from coal, NaCl is a major constituent of the vapor phase. Two experiments were performed with pellets of KaoK subjected to an unsaturated NaCl vapor. The configuration was slightly different for the two experiments. Figure 6.6-50 shows the configuration (#1) for the first experiment (sample A) which did not use the humidifier. KaoK sample A was kept at 800°C, and the NaCl source was at 784°C with a dry N₂ purge. The second configuration (#2) allowed for continuous KaoK pellet mass measurement and introduction of simulated flue gas purge (Punjak et al. (1989) and Uberoi et al. (1990)). Sample B was kept at 800°C, and the source was at 780°C. The purge contained 80% N₂, 15% CO₂, 3% O₂, and 2% H₂O.

Seven elements were measured in the KaoK sample by AA analysis: Al, Si, Ca, Fe, Na, K, and Mg. The mass per gram of original sample of Al, Si, Fe, and Mg in all the KaoK samples were found to be unaffected by heating and presence of an Na source. Ca levels were too small to draw any conclusions. The ratio of moles of alkali to moles of (Al+Si) shown in Figure 6.6-51, displayed an increase in Na and a decrease in K for both samples A and B. It is clear that NaCl vapor could allow for removal of K from KaoK pellets both in the presence and absence of moisture. It not clear if K removal was due to Na or Cl. Potassium was lost only in cases where sodium was gained which suggests, but does not confirm, K displacement by Na. Exchange of Na for K was not one-for-one, also water vapor was not necessary for displacement to occur. This was in contrast to sodium

FIGURE 6.6-50. - Reactor #1 for potassium displacement experiments.

FIGURE 6.6-51. - Ratio of alkali to Al + Si for KaoK.

capture results reported by Punjak et al. (1989) and Bachovchin et al. (1986) that suggested moisture was important for capture of Na by kaolinite and emathlite respectively. Apparently Na capture with K displacement is a different mechanism than Na capture alone.

6.6.3.3.2 Potassium Displacement Experiments with Illite

Potassium was lost from kaolinite impregnated with K in the presence of NaCl vapor. It was of interest, however to examine a naturally occurring potassium rich aluminosilicate. Bench scale experiments were conducted with illite, a potassium rich mineral common in many coals.

Illite clay pellets were prepared by the same technique used for KaoK. The mass of Al, Si, Fe, and Mg per gram of original sample showed no change during each of the illite experiments. This was consistent with the KaoK results.

A third experimental configuration (#3) was used with illite pellets and is shown in Figure 6.6-52. A third configuration was required to enhance transport of vapor Na species other than NaCl to the illite pellet. Reaction of sodium species (other than NaCl) with quartz source bowls and reactor walls was very fast and reduced the concentration of sodium in the vapor. The inside diameter of the tube holding the source and sorbent in configuration #3 was approximately 7 mm. Table 6.6-6 summarizes the experimental conditions and configuration used for each illite sample, and Table 6.6-7 lists the average unreacted illite composition.

FIGURE 6.6-52. - Configuration #3 for illite experiments.

TABLE 6.6-6. - Summary of illite bench scale experiments

Illite Sample	Illite Temp (°C)	Source, Temp (°C)	Purge	Time (min)	Exper. Config.*
B	-	-	-	-	-
E	1000	-	-	30	-
F	800	NaCl 780	N ₂	1532	#1
ZA	790	-	N ₂ , H ₂ O _(v) , HCl _(v) [†]	969	#1
ZB	800	Na ₂ SO ₄ 796 [‡]	N ₂ , H ₂ O _(v)	1500	#3
ZC	790	Na ₂ SO ₄ 800	N ₂ , H ₂ O _(v)	1480	#3
XA	800	Na ₂ SO ₄ 805	N ₂ , H ₂ O _(v)	1762	#3
XB	800	Na ₂ SO ₄ 805	N ₂ , H ₂ O _(v) , HCl _(v) [†]	1700	#3
V	790	Na ₂ SO ₄	N ₂	32	#1
W	790	NaOH	N ₂	30	#1

#1 - Configuration shown in Figure 6.6-50.
#3 - Configuration shown in Figure 6.6-52.
[†]approximately 0.03 N HCl in humidifier at > 25°C.
[‡]stainless steel foil sheath surrounded area between source and sorbent.

TABLE 6.6-7. - Average illite composition

Element	g/g Illite	Standard Deviation g/g
Al	0.0895	0.0015
Si	0.2526	0.0072
Ca	0.0025	0.0013
Fe	0.0411	0.0037
Na	0.0045	0.0001
K	0.0343	0.0065
Mg	0.0120	0.0003

Only sample F with a NaCl source showed significant K release (Figure 6.6-53). Sample ZA had HCl in the humidifier and showed no K release. Sample XB had HCl in the humidifier and a Na₂SO₄ source also showed no K release. Since no Na capture was noted in this experiment, it is suspected that Na vapor concentrations were very low. To overcome experimental difficulties in keeping reactive sodium in the vapor long enough to reach the illite pellet, samples V and W mixed the sodium source directly with illite powder. Samples V and W mixed Na₂SO₄ and NaOH with illite and a few drops of deionized water. The samples were then placed in the hot reactor. These experiments would be considered worst case scenarios with respect to sodium concentration. Sodium was apparently captured in samples V and W, but potassium was not displaced. Sodium was captured in sample ZB which used a stainless steel foil sheath to protect the quartz reactor tube. In this experiment the stainless steel was extremely corroded. From bench scale experiments with illite we can conclude that NaCl can allow for K release. Neither Cl or Na alone will release K, and also Na vapor can be captured by illite.

Energy dispersive x-ray analysis (EDX, Applied Materials Laboratory, University of Arizona) did not detect Cl in samples exposed to NaCl and HCl. Profiles of K and Na in both illite and KaoK pellets ($\approx$ 150 to 300 μ m thick) were flat. This suggested that transport was not limiting under the experimental conditions used.

FIGURE 6.6-53. - Results of illite experiments.

6.6.3.4. Conclusions

A summary of potassium behavior during pulverized coal combustion is given below. Also included are conclusions from both laboratory combustion and bench scale experiments.

- Low-rank coals Beulah Lignite and Loy Yang 2301 showed a significant fraction of the potassium in the small size classes of sampled fly ash. This could be due to the original form of the potassium being easily vaporized, or the high sodium content of both coals. These two coals suggested a positive correlation between potassium vaporization and chlorine content.
- Bituminous coals in this study showed a very small fraction of the potassium in the small size classes of sampled fly ash. This is consistent with the potassium existing primarily in mineral matter. No correlation was found for the bituminous coals between potassium vaporization and chlorine content.
- A correlation was found between the fraction of vaporized sodium and potassium. Since the original form of potassium was likely bound to mineral matter, this suggested that sodium could enhance potassium vaporization.
- Potassium vaporization was enhanced significantly in Kentucky No. 11 (high illite content, low sodium and chlorine content) in the presence of extraneous sodium acetate. The vaporization was lower than for Beulah Lignite that had a similar sodium-to-silicon ratio.

- Sodium chloride vapor allowed for release of potassium from mineral matter in both illite and kaolinite impregnated with potassium. More sodium was captured than potassium was released suggesting that displacement was not one-for-one.
- Potassium was not released in the presence of sodium or chlorine alone at the low temperatures of the bench experiments. Potassium vaporization was enhanced by Na alone at higher temperatures, however (doped Kentucky #11 experiments).

6.6.4 Dispersed Calcium Transformations

Fraction oxide plots discussed in Section 6.5 showed the calcium behavior to be variable. For Beulah Lignite, Illinois No. 6, Kentucky No. 9, and Kentucky No. 11 there was a slight enrichment of calcium in the size class between 0.43 and 5.8 μm . Loy Yang, which was low in calcium, showed no significant contribution of calcium in any measured size class. Eagle Butte showed significant enrichment of calcium increasing as the size class decreased.

Results from CCSEM analysis showed two distinct compositions involving of calcium in the largest particles ($\geq 9 \mu\text{m}$) for Beulah Lignite (Figure 6.5-163) and Eagle Butte sub-bituminous (Appendix I). In Ca versus Si plots, two frequent Ca compositions appeared as a peak of 50% Ca, 25% Si, and another of nearly 100% Ca. As size decreased to 2.2 and 0.65 μm (Figures 6.5-165 and 6.5-166), the bimodal composition distribution was replaced by a single Ca composition (40% Ca, 15% Si) for both Eagle Butte and Beulah Lignite. The latter Ca composition mode, found in large and small particles, was indicative of a calcium silicate. The 100% Ca mode was determined to be CaO by X-ray absorption near edge structure analysis (Huffman et al. (1990)).

Two observed compositions in the large sizes might suggest that calcium existed in the parent coal in two distinct forms: one forming large CaO particles and the other forming calcium silicate in small and large particles. However, this is not the case for either Beulah Lignite or Eagle Butte.

Calcium in Beulah Lignite parent coal did not exist in silicate mineral matter nor as calcite. Mineralogical analysis did show "macerals richer than average in S or Ca" listed as 10% of the mineral matter (Sections 3 and 4). Beulah Lignite also contained a large concentration of acid-soluble calcium. Both observations implied that calcium existed as small inclusions or organically bound in the parent coal. Huffman et al. (1990) claimed that "in lignite, calcium is molecularly dispersed in coal macerals and is bonded to the oxygen anions in carboxyl groups". Therefore, some mechanism allows for the formation of large CaO particles from highly dispersed calcium (small CaO particles were not detected). The mechanism must also account for the formation of calcium silicates in all size ranges.

During char formation in nitrogen (i.e. in the absence of oxygen), Radović et al. (1983) showed the formation of small CaO particles from dispersed calcium of "demineralized North Dakota lignite loaded with 2.9 wt% Ca by ion exchange". At 1275 K

Radović et al. showed that calcium remained highly dispersed for short residence times (0.3 to 1.5s). For longer residence times (from 5 min. to 1 hour) small CaO particles formed in the char. Particle size also increased with longer residence times from 0.0245 to 0.028 μm . These sizes were, however much smaller than sizes ($> 9 \mu\text{m}$) detected by CCSEM analysis for coal ash. This was consistent with Huggins et al. (1988) who studied the state of calcium in pyrolysed char and showed that for rapidly pyrolysed chars, calcium remained highly dispersed. For chars prepared by slow pyrolysis, "significant fractions of the calcium had transformed to bulk CaO." Although CaO was formed, large particles were not observed. It can be concluded that large CaO particles are not created during char formation in the absence of oxygen.

Nankervis and Furlong (1980) used a low temperature ashing procedure to produce North Dakota lignite carbon-free ash. The carbon-free ash was then heated to study phase changes in the ash. Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) was formed, and at higher temperatures akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) appeared. No CaO particles were reported. Calcium sulphate was reported at the lower temperatures but was attributed to an artifact of the ashing procedure. Calcium silicate was formed when heating carbon-free ash. The absence of large CaO particles in the carbon-free ash and also during char formation suggests that the formation of large CaO particles is linked to the receding of the carbon matrix during burnout.

Graham, et al. (1990) performed experiments and modeling of submicron calcium fly ash formation. The mechanism studied was reduction of CaO within char and subsequent escape of a reduced Ca gas. Their work suggested that CaO reduction was negligible below 2000 K. The maximum measured gas temperature for the Beulah Lignite burn corresponding to CCSEM samples reported in this study was approximately 1570 K. Char particle temperatures might have been higher by a maximum of approximately 200 K (Scotto (1988)), and the thermocouple might have measured low due to radiation losses by a maximum of approximately 50 K (Bose (1989)). Even with these large corrections, the char temperature was less than 1850 K. This implied that production of a reduced Ca gas within the char was not significant. This indicates that vaporization of calcium is responsible neither for the formation of large CaO particles nor in the reaction of calcium with silicates.

Quann and Sarofim (1986) performed a scanning electron microscopy study of partially burned chars of a lignite. The Montana lignite contained calcium which was primarily organically bound (highly dispersed). Their study showed small ($\sim 1 \mu\text{m}$) calcium rich (also with magnesium, aluminum and sulfur) particles on the surface of chars at an early stage of burnout. As burnout progressed, the calcium particles grew. Micrographs of chars at a later stage of burnout indicated sizes of approximately 5 μm . At early stages of burnout, particles on the exterior surface of the chars were relatively devoid of silicon, but those at extensive char burnout were associated with silicon. They concluded that organically bound Ca (and Mg) released as the char burned away and agglomerated to form large particles.

The calcium behavior can be summarized by the following observations:

CCSEM results for Beulah Lignite and Eagle Butte ash showed a bimodal calcium composition distribution in the large sizes ($> 9 \mu\text{m}$). The two modes corresponded to CaO and gehlenite.

- Only the gehlenite composition was observed in the smaller sizes (between 0.43 and 4.7 μm). No small CaO particles were observed.
- Nearly all the Ca in Beulah Lignite (and a significant fraction in Eagle Butte) was organically bound (highly dispersed).
- Organically bound Ca remains highly dispersed or forms CaO particles less than 0.03 μm in size during char formation.
- Carbon-free Beulah Lignite ash forms gehlenite, but no CaO particles.
- Vaporization of a reduced Ca gas was insignificant during combustion of Beulah Lignite in this study.
- At early stages of burnout, 1 μm calcium rich particles formed on the external surface of the char. At later stages of burnout these particles grew to 5 μm .
- At early stages of burnout, CaO particles on the exterior char surface were relatively devoid of silicon. At extensive burnout the exterior particles were associated with silicon.

Observation of large CaO particles can be explained in the following way. Large CaO particles are not formed during char formation nor in a heated carbon-free ash. In the absence of burnout, Ca remained either highly dispersed or formed particles much smaller than those observed in Beulah Lignite ash. Formation of large CaO particles is linked to receding of the char matrix during burnout. Finely dispersed Ca releases from the organic matrix as it burns away and adheres to the external surface of the char. As the char surface recedes, Ca agglomerates forming larger particles. Shedding of large CaO particles or perimeter fragmentation of outer layers of char during burnout (Beér (1988)) would prevent intimate contact of external Ca with included silicates found deeper in the char. Such contact was allowed in the studies of Nankervis and Furlong (1980) and gehlenite was formed, but no CaO particles were reported. Absence of CaO particles in the small size classes ($< 4 \mu\text{m}$) suggests that either a critical size is reached before shedding of large particles occurs, or that smaller CaO reacts rapidly with aluminosilicates to form calcium aluminosilicates.

Formation of calcium silicates was the result of agglomeration of calcium with included silicates (kaolinite in the case of Beulah Lignite) as the char surface receded. The specific Ca-Si composition shown in CCSEM results was suggestive of a chemical reaction. It can be concluded that agglomeration of Ca with kaolinite was followed by chemical reaction allowing only a specific composition to be observed by CCSEM. Calcium silicate compositions measured in Beulah Lignite ash were consistent with gehlenite formation. Char fragments which contained dispersed calcium and included silicates would form smaller particles of calcium silicate. This would result in the single composition found in the smaller size classes.

6.7 Mechanistic Model of Alkali Behavior

This section interprets alkali behavior mechanistically. In Subsection 6.7.1 raw data of impactor alkali distributions is manipulated to deduce the fraction of alkali that could participate in condensation from the bulk gas phase. This quantitative evaluation of impactor distributions is compared to model predictions described in Subsection 6.7.2. Modelling of sodium behavior suggested a dependence on silicates present, the form of sodium in coal, and on char burnout kinetics. A table of nomenclature is included at the end of each section.

6.7.1 Interpretation of Size Segregated Ash Composition Data

Impactor data has suggested vaporization of sodium and potassium during pulverized coal combustion. The fraction of alkali on plate 8 and the after-filter, f_{gA} , has been used as a qualitative measure of the fraction of alkali that has vaporized. Although f_{gA} might be a good qualitative measure, a more quantitative measure was desired for engineering calculations and comparisons to predictive models. A method for extracting the fraction of alkali vaporized from impactor data based on work by Neville and Sarofim (1985) was developed below. The method assumed that a fraction of the alkali was captured and was fixed in the ash. The fraction not captured was assumed to participate in condensation on existing fly ash particles.

Previous work has shown that sodium can be captured by aluminosilicates and silica during pulverized coal combustion thus making it unavailable for condensation (Wibberly and Wall (1982), Lindner and Wall (1988), Huffman et al. (1990), Helble et al. (1990), Raask (1985)). Work by Lindner and Wall (1990) suggested that aluminosilicates were more efficient than silica at capturing sodium. This was consistent with work by Punjak et al. (1989), and Uberoi et al. (1990), which showed kaolinite as being more efficient than bauxite and emathlite at scavenging vaporous sodium chloride. However, due to the large quantity present in many coal systems, silica may account for a significant portion of captured sodium. CCSEM data on fly ash discussed in Subsection 6.5 showed that although capture occurred for both kaolinite and quartz in the largest size classes, not all the kaolinite and quartz present participated in sodium capture.

6.7.1.1 Mathematical Development

Since the largest size class had unreacted kaolinite and silica, and since other non-alkali species may be competing for silicates, it was difficult to characterize the distribution of captured alkali. From this argument, the fraction of alkali captured in a size range from x to $x + dx$ could not be assumed proportional to silicate mass in that size range as was done by Neville and Sarofim (1985). Characterizing the distribution of captured potassium was even more difficult since it existed primarily in the mineral matter prior to combustion. Instead of assuming a distribution, the fraction of captured alkali in an ash particle size range from x to $x + dx$ was characterized by an unknown distribution function $R(x)$.

Alkali was assumed to vaporize and participate in condensation on existing fly ash particles and also participate in homogeneous nucleation. The fraction of alkali vaporized was divided into two terms, θ and f_0 . A portion of the vaporized alkali was assumed to condense on existing fly ash particles using the continuum assumption. This fraction was defined by θ in g sodium vaporized per g total sodium. The second term, f_0 , was the fraction of sodium which vaporized and participated in condensation governed by free molecular kinetics, and homogeneous nucleation. The fraction characterized by f_0 was in a size range smaller than x^* .

Given the total mass of alkali in an impactor sample, m_{Alk} , the mass of alkali captured would be given by $(1-\theta-f_0)m_{\text{Alk}}$. The concentration of captured alkali in the size range from x to $x + dx$ in g alkali per g ash would then be given by $C_c(x)$.

$$C_c(x) = \frac{(1-\theta-f_0)m_{\text{Alk}}R(x)}{\frac{\pi}{6}\rho n(x)x^3} \quad (6.24)$$

where $\rho(\pi/6)n(x)x^3$ is the mass of ash in the size range from x to $x + dx$.

The rate of condensation of vaporized alkali on an existing fly ash particle is approximated by the Fuchs-Sutugin relationship.

$$F(x) = \frac{2\pi D(P-P_{\text{eq}})x}{RT} \left[\frac{1 + \text{Kn}}{1 + 1.71\text{Kn} + 1.33\text{Kn}^2} \right] \quad (6.25)$$

The rate of molar transfer to a particle is given by $F(x)$ in moles per second. The Knudsen number was given by Kn , D is the alkali diffusivity, P was the alkali partial pressure in the bulk flue gas and P_{eq} was the alkali vapor pressure at the particle surface.

The concentration of alkali in the size range from x to $x + dx$ is given by $C(x)$ for sizes larger than x^* which does not include f_0 . The first term in the equation for $C(x)$ accounted for alkali capture by non-alkali species, and was written above as $C_c(x)$. Condensation on particles greater than x^* in size is accounted for by the second term. The second ratio in the second term is the fraction of condensed alkali that was in the size range from x to $x + dx$.

$$C(x) = \frac{(1-\theta-f_0)m_{\text{Alk}}R(x)}{\frac{\pi}{6}n(x)\rho x^3} + \frac{\theta m_{\text{Alk}}}{\frac{\pi}{6}n(x)\rho x^3} \frac{F(x)n(x)}{\int_{x^*}^{\infty} F(x)n(x)dx} \quad (6.26)$$

The equation for $C(x)$ is a continuous function of the concentration of alkali in ash in g sodium per g ash for fly ash particles of sizes greater than x^* . However, it is required that

the equation be derived to give the response of an impactor plate. Instead of focussing on a size range from x to $x + dx$, the range would be x_i to x_{i+1} for plate i . Multiplying both sides of the equation for $C(x)$ by the ash mass distribution and integrating yields:

$$\frac{\pi}{6m_{\text{Alk}}} \int_{x_i}^{x_{i+1}} \rho C(x) n(x) x^3 dx = (1 - \theta - f_9) \int_{x_i}^{x_{i+1}} R(x) dx + \theta \frac{\int_{x_i}^{x_{i+1}} F(x) n(x) dx}{\int_{x^*}^{x_m} F(x) n(x) dx} \quad (6.27)$$

The distribution of captured alkali, $R(x)$, becomes $R(x_i)$ the fraction of captured alkali on impactor plate i . The mass of captured alkali on impactor plate i is defined as $m_c(x_i)$.

$$m_c(x_i) = (1 - \theta - f_9) m_{\text{Alk}} R(x_i) \quad (6.28)$$

The second term of the equation for $C(x)$ accounts for condensed alkali in the ash. Defining $m_v(x_i)$ as the mass of condensed alkali on impactor plate i , an equation can be derived analogous to the equation for $m_c(x_i)$.

$$m_v(x_i) = \theta m_{\text{Alk}} \left[\frac{\int_{x_i}^{x_{i+1}} F(x) n(x) dx}{\int_{x^*}^{x_m} F(x) n(x) dx} \right] \quad (6.29)$$

Condensation is assumed to occur in a continuum such that $Kn \ll 1$, and $F(x)$ is proportional to x for $x > x^*$. Also, neglecting the size dependence of P_{eq} for $x > x^*$ (neglecting the Kelvin effect) an equation for $m_v(x_i)$ can be written.

$$m_v(x_i) = \theta m_{Alk} \left(\frac{\int_{x_i}^{x_{i+1}} \frac{2\pi D}{RT} (P - P_{eq}) x n(x) dx}{\int_{x^*}^{x_m} \frac{2\pi D}{RT} (P - P_{eq}) x n(x) dx} \right) \quad (6.30)$$

This also assumes that capture is not film diffusion limited. The number distribution inside the integral can be approximated by the ash mass distribution, m_a , divided by the volume.

$$m_v(x_i) = \theta m_{Alk} \left(\frac{\int_{x_i}^{x_{i+1}} x m_a(x)/x^3 dx}{\int_{x^*}^{x_m} x m_a(x)/x^3 dx} \right) \quad (6.31)$$

Taking advantage of the mean value theorem and approximating a size in the interval from x_i to x_{i+1} by x_i yields an equation for $m_v(x_i)$, where m_{ai} is the mass of ash on plate i .

$$m_v(x_i) = \theta m_{Alk} \left(\frac{m_a/x_i^2}{\sum_{i=1}^8 m_a/x_i^2} \right) \quad (6.32)$$

The continuum assumption was made only for impactor plates 1 through 8. Plate 1 represents the largest size class in the impactor and plate 8 the next to smallest size class.

Using the definitions of $m_c(x_i)$ and $m_v(x_i)$ and dividing by m_{Alk} an equation for $f_i = m(x_i)/m_{Alk}$, the fraction of alkali on stage i , can now be written for $i = 1, \dots, 8$.

$$f_i = (1 - \theta - f_p) R(x_i) + \theta \left(\frac{m_a/x_i^2}{\sum_{i=1}^8 m_a/x_i^2} \right) \quad (6.33)$$

The equation for f_i was valid for impactor stages 1 through 8. The after-filter, represented by f_9 , was assumed to have only condensed and nucleated alkali, with negligible capture, ie it was assumed that $R(x_9)$ was zero. This assumption was verified for Beulah Lignite shown below.

The equation for f_i represents eight equations with nine unknowns: the eight $R(x_i)$ and θ . Impactor data have suggested that the mass of silicate matter on impactor stage 8, and thus capture, was relatively small. Assuming that capture on stage 8 was negligible, and that the presence of alkali on this stage was dominated by condensation allowed for a fully determined set of equations.

$$\bar{f} = (1-\theta-f_9)\bar{R} + \theta\bar{Z} + f_9\bar{I}_9 \quad \text{for } i=1,\dots,9 \quad (6.34)$$

$$\bar{R}^t = (r_1, r_2, \dots, r_6, r_7, 0, 0) \quad (6.35)$$

$$\bar{Z}^t = (z_1, z_2, \dots, z_6, z_7, z_8, 0) \quad (6.36)$$

$$\bar{I}_9^t = (0, 0, \dots, 0, 0, 0, 1) \quad (6.37)$$

where $\bar{R}$ is a vector of unknowns characterizing the distribution of captured alkali, $\bar{Z}$ is a vector of known elements characterizing the distribution of condensed alkali under the continuum assumption defined by Eq. (6.34), and $\bar{I}_9$ is a unit vector corresponding to the after-filter.

The assumption of condensation taking place in a continuum was made for $Kn \ll 1$. Stage 8, the last stage of the impactor, has a cutoff diameter of $0.43 \mu\text{m}$. At 1000°C Kn is estimated at 1.3 for a $0.43 \mu\text{m}$ particle. The continuum assumption is not valid for sizes below stage 8 found on the after-filter. Another assumption was that the Kelvin effect was not important for sizes larger than $0.43 \mu\text{m}$. The Kelvin effect is expected to be important for sizes less than $0.3 \mu\text{m}$ which were collected on the impactor after-filter (Neville and Sarofim (1985)). Particles which were created by nucleation are expected to be collected on the after-filter. For these reasons, only the top eight stages were included in the portion of vaporized alkali expected to follow condensation kinetics governed by the continuum assumption.

6.7.1.2 Results

Since capture on stage 8 was assumed negligible (verified below for Beulah Lignite), θ could be determined explicitly.

$$\theta = f_9/z_8 \quad (6.38)$$

Each of the R_i ($i < 8$) could then be determined using this value of θ .

$$R_i = \frac{(f_i - \theta z_i)}{(1 - \theta - f_9)} \text{ for } i = 1, \dots, 7 \quad (6.39)$$

The total fraction of alkali which could participate in condensation and nucleation was then $\theta + f_9$.

Figures 6.7-1 and 6.7-2 show a linear correlation between $\theta + f_9$ and f_{8A} for Na and K for six coals. The three points in the upper right corner of the plots are for Loy Yang which does not follow the linear correlation. The concentration of alkali in the ash for both Loy Yang coals was very high, and the above analysis is not expected to apply. Implicit in the mathematical development is that, once condensation begins, $n(x)$ is not a strong function of time in any size class. This assumes that coagulation and fragmentation are negligible, and that the condensate forms only a thin film on the fly ash particles. For Loy Yang, with a high concentration of condensate, a thin film assumption is not valid. Figures 6.7-1 and 6.7-2, however show that f_{8A} is lower than $\theta + f_9$ (Table 6.7-1), but is a good measure of the trend of alkali vaporization.

FIGURE 6.7-1. - $\theta + f_9$ versus f_{8A} for Na.

FIGURE 6.7-2. - $\theta + f_g$ versus f_{gA} for K.

TABLE 6.7-1. - Fraction of condensed sodium (data also included in Figure 6.7-1)

Sample	Peak T (K)	% of sodium condensed	
		$\theta + f_g$	$f_g + f_g$
38 A Beu Lig	1560	17.27	6.57
38 B Beu Lig	1405	26.74	14.55
38 C Beu Lig	1405	19.02	9.14
36 A Kent #9	1648	1.42	0.32
36 B Kent #9	1510	4.27	0.88
36 C Kent #9	1510	2.04	0.68

A comparison of the above method to solubility data can be made with data from burn 42. Burn 42 used Loy Yang doped with kaolinite which lowered f_{gA} for sodium from approximately 75% to 12%. The solubility analysis dissolved half an impactor sample with deionized water, and half was subjected to dissolving acid. The water soluble portion was considered representative of condensed as opposed to reacted alkali. The water insoluble portion, representative of captured alkali, was the difference between acid dissolved and water soluble alkali. Previous analysis (Subsection 6.6.2) showed that a significant fraction of the mass on plate 8 and the after-filter was silicon, but that nearly all of the sodium was water soluble. This suggests that although silicates were present in this size range, capture of sodium was negligible.

Figures 6.7-3 and 6.7-5 show results for sodium using the analysis method developed above for two samples collected during burn 42. Figures 6.7-4 and 6.7-6 show results of the solubility analysis. The lower bar in the stacked bar charts represents captured sodium, and the upper bar represents condensed sodium. The sum of the captured and condensed alkali was the total fraction of alkali on a given stage, and the fraction of water soluble or condensed alkali is given in parentheses.

FIGURE 6.7-3. - Model results for sample 42A sodium.

FIGURE 6.7-4. - Solubility results for sample 42A sodium.

FIGURE 6.7-5. - Model results for sample 42B sodium.

FIGURE 6.7-6. - Solubility results for sample 42B sodium.

With the exception of results for impactor plate 1, the model compared well with data. The reason for the discrepancy for stage 1 was not readily apparent. Waterglass, a possible reaction product of sodium with quartz, is soluble in water but Loy Yang did not contain a large fraction of quartz (0.18% dry basis). It was expected that kaolinite additive (9.82% db) would dominate the impactor sample.

Figures 6.7-7 and 6.7-9 show model results applied to potassium from burn 42. Figures 6.7-8 and 6.7-10 show solubility analysis results. The model still underpredicts condensable alkali on stage 1, but comparison for K was better than for Na.

Figure 6.7-11 shows that the distribution of captured Na is nearly linear with the distribution of silicon for impactor plates 2 through the after-filter. Including impactor plate 1, however shows a significant change in slope for both model and solubility data (Figure 6.7-12). The assumption that the distribution of captured sodium is linear with silicon distribution, as was done by Neville and Sarofim (1985), is valid for plates 2 through the after-filter, but not for plate 1.

Using the above analysis, model results for burn 38 (Beulah Lignite) are shown in Figures 6.7-13 and 6.7-14. Figures 6.7-15 and 6.7-16 show results from burn 40 Eagle Butte. Sample A for both burns was for a different temperature profile than for samples B and C. Results showed that an increasing fraction of alkali mass was condensed as size decreased. Sample B for Beulah Lignite, however showed a negative fraction of capture at stage 7. Consistent with solubility results for burn 42, results for burns 38 and 40 suggested that the assumption of negligible capture by silicates on stage 8 was reasonable.

FIGURE 6.7-7. - Model results for sample 42A potassium.

FIGURE 6.7-8. - Solubility results for sample 42A potassium.

FIGURE 6.7-9. - Model results for sample 42B potassium.

FIGURE 6.7-10. - Solubility results for sample 42B potassium.

FIGURE 6.7-11. - Captured Na versus Si distribution plates 2-Af.

FIGURE 6.7-12. - Captured Na versus Si distribution plates 1-Af.

FIGURE 6.7-13. - Model results for burn 38 sodium.

FIGURE 6.7-14. - Model results for burn 38 potassium.

FIGURE 6.7-15. - Model results for burn 40 sodium.

FIGURE 6.7-16. - Model results for burn 40 potassium.

Figure 6.7-17 shows the results for six coals: (A) Kentucky No. 9, (B) Kentucky No. 11, (C) Upper Freeport, (D) Illinois No. 6, (E) Eagle Butte, and (F) Beulah Lignite. Results showed that the lower rank coals (Beulah Lignite and Eagle Butte) had the highest fraction of condensible alkali.

Comparison of the above analysis to water solubility data suggested that the condensation model underpredicts the fraction of condensed alkali primarily in the largest size class, but shows good agreement in the smaller size classes. A pure condensation model, such as the one developed above, would also be expected to underpredict the actual fraction that vaporized since a portion of the alkali can vaporize and subsequently chemically react. If the gas phase transport were not the limiting mechanism then this vaporized alkali would not be included in the fraction of condensible alkali θ . The condensation model does not restrict itself to a captured alkali distribution which is linear with the silicon distribution. This allows for application to other aerosol systems.

FIGURE 6.7-17. - $\theta + f_g$ for K and Na for six coals.

Nomenclature for Subsection 6.7:

$C(x)$	concentration of alkali in ash [g alkali/g ash],
$C_c(x)$	concentration of captured alkali [g alkali/g ash],
D	alkali diffusivity [cm^2/s],
$F(x)$	flux of alkali to particle [mol/s],
f_i	fraction of alkali on plate i ($9 = \text{after-filter}$),
Kn	Knudsen number,
$m_a(x)$	ash mass distribution [$\text{g}/\mu\text{m}$],
m_{ai}	ash mass on plate i [g],
m_{Alk}	total mass of alkali in an impactor sample [g],
m_c	mass of captured alkali [g],
m_v	mass of condensed alkali [g],
$n(x)$	ash number distribution in the impactor [$\#/\mu\text{m}$],
P	partial pressure of alkali in gas phase [Pa],
P_{eq}	vapor pressure of alkali at particle surface [Pa],
R	gas constant [J/K/mol],
$R(x)$	distribution of captured alkali [μm^{-1}],
R_i	fraction of captured alkali on plate i ,
T	temperature [K],
x	aerodynamic size [μm],
x^*	minimum size governed by continuum mechanics [μm],
θ	fraction of alkali vaporized and condensed under the continuum assumption,
ρ	ash density [g/cm^3].

6.7.2 Modelling Sodium Capture by Silicates During Pulverized Coal Combustion

Sodium behavior in combustion systems varies with respect to combustion conditions and coal selection. Figure 6.7-18 shows the fraction of sodium in the vapor (f_{vNa}), represented by $\theta + f_9$ developed in Subsection 6.7.1, for six coals as a function of measured peak temperature. Although the stoichiometric ratio (SR) varied slightly it was approximately 1.2 for each experiment, and the peak temperature was nearly representative of experimental conditions (including time-temperature history, coal loading, and char burnout times). Figure 6.7-18 shows highly variable behavior that, taken as a whole, shows no apparent trends. However, for low-rank coals (Beulah Lignite, Loy Yang brown, and Eagle Butte sub-bituminous) f_{vNa} decreased with increasing temperature. This was consistent with experiments on Montana Lignite by Neville and Sarofim (1985). In contrast, higher-rank bituminous coals (Illinois No. 6, and Kentucky No. 11) showed f_{vNa} increasing with temperature. To better understand the variable Na behavior a model of Na capture by silicates was developed below.

FIGURE 6.7-18. - Fraction of condensable sodium measured in the cascade impactor as a function of measured peak temperature for six separate coals.

The model allows for release of Na from a shrinking char particle, and includes Na capture by silicate minerals. Reaction between Na and silicates is based on work by Punjak et al. (1989) and Uberoi et al. (1990), but allows for capture of NaOH instead of NaCl (Subsection 6.6.2, and Appendix E). Silicates were assumed to be of two types: kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$) which forms metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) upon heating, and quartz (SiO_2). Equilibrium calculations (Subsection 6.6.1) suggested sodium disilicate ($\text{Na}_2\text{O} \cdot 2\text{SiO}_2$) as a reaction product of sodium with quartz (Eq. (6.41)).

6.7.2.1 Governing Equations

6.7.2.1.1 Inside the Char Particle

Figure 6.7-19 shows a schematic diagram of "mobile" Na diffusing to a char particle surface, and escaping to the bulk flue gas. Equation (6.42) describes diffusion and reaction of a volatile species C_a (g/cm^3 char) as it migrates to the surface of a shrinking spherical

FIGURE 6.7-19. - Schematic diagram of sodium diffusion through a shrinking char particle.

particle. A homogeneous source of C_a exists due to Na bound to the char matrix, C_s , releasing to the mobile state. Reaction of C_a with silicates includes interphase (between porous char matrix and silicate particles) and intraphase (inside silicate particles) mass transfer.

$$\frac{\partial C_a}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_a}{\partial r} \right) - C_a \sum_{i=1}^n \frac{\eta_i k_{si} S_i k_{mi} C_i}{\eta_i k_{si} S_i C_i + k_{mi}} + k_s C_s \quad (6.42)$$

$$C_a = 0, \quad R = R_0 \quad \text{at } t = 0 \quad (6.43)$$

$$\frac{\partial C_a}{\partial r} = 0 \quad \text{at } r = 0 \quad (6.44)$$

$$-D \frac{\partial C_a}{\partial r} = k_{mb} (C_a - C_b) - C_a \frac{dR}{dt} \quad \text{at } r = R(t) \quad (6.45)$$

Equation (6.45) matches mass fluxes at the char surface.

Release of bound volatile, C_s , is governed by a first order reaction (Equation (6.46)). The second term on the right-hand-side, often overlooked in previous developments, accounts for release of C_s from char, initially of radius R_0 , due to shrinking to a minimum radius R^* . C_s (g/cm³ char) is bound only to the organic fraction of char.

$$\frac{dC_s}{dt} = -k_s C_s + \frac{C_s R^{*3}}{(R^3 - R^{*3})} \frac{3}{R} \frac{dR}{dt} \quad (6.46)$$

$$C_s = C_{s0} \quad \text{at } t = 0 \quad (6.47)$$

Each inherent silicate i (g/cm³ char) can react with migrating volatile C_a (Eq. (6.48)).
Interphase mass transfer

$$\frac{\partial C_i}{\partial t} = -\frac{\beta_i \eta_i k_{ai} S_i k_{mi} C_i C_a}{\beta_i \eta_i k_{ai} S_i C_i + k_{mi}} - \frac{C_i}{V} \frac{dV}{dt} \quad (6.48)$$

$$C_i = f_i C_{Si0} \quad \text{at } t = 0 \quad \text{for } i = 1, \dots, n \quad (6.49)$$

is modelled by a mass transfer coefficient k_{mi} . An effectiveness factor η_i allows for intraphase mass transfer resistance, k_{ai} is the intrinsic reaction rate coefficient, S_i is silicate specific area, and β_i accounts for stoichiometry. Initially the internal area is available for reaction. After fusing at temperature T_{mi} , only external area is available. Each subscript i allows for different silicate species or a distribution of sizes. No loss of included silicates to the bulk phase is allowed for, and silicates are modeled as redistributing homogeneously as the char shrinks. At burnout there is one ash particle per char particle. Equation (6.49) states that C_i is initially a fraction, f_i , of the initial concentration of included silicate species, C_{Si0} .

6.7.2.1.2 Outside the Char Particle

Na concentration in the bulk, C_b (g/cm³ gas), increases due to C_a escaping the char (first term on the right-hand-side of Equation (6.50)). The second term accounts for reactions of C_b with extraneous silicates C_j . This reaction term, analogous to the reaction term inside the char, includes interphase (bulk gas phase to silicate particle) and intraphase (inside the silicate particle) mass transfer. The third term in Equation 6.27 allows for increase in C_b due to char shrinkage. Both C_s and C_a can escape the char by this mechanism. The fourth term accounts for temperature effects on the bulk gas volume, and initially no volatile is in the gas phase.

$$\frac{dC_b}{dt} = k_{mb} a_v (C_a|_{r=R(t)} - C_b) - C_b \sum_{j=1}^n \frac{\eta_j k_{aj} S_j k_{mj} C_j}{\eta_j k_{aj} S_j C_j + k_{mj}} - (C_s + C_p) \frac{dR}{dt} a_v - \frac{C_b}{V_b} \frac{dV_b}{dT} \frac{dT}{dt} \quad (6.50)$$

$$C_b = 0 \quad \text{at } t = 0 \quad (6.51)$$

Reaction of C_j is modelled using Eq. (6.52). It is analogous to Eq. (6.48) for included silicates except the bulk volume, V_b , changes with respect to temperature as an ideal gas. Equation (6.53) states that initially C_j (g/cm³ flue) is a fraction, g_j , of the total initial concentration of all extraneous silicates, C_{sj0} .

$$\frac{dC_j}{dt} = - \frac{\beta_j \eta_j k_{aj} S_j k_{mj} C_j C_b}{\beta_j \eta_j k_{aj} S_j C_j + k_{mj}} - \frac{C_j}{V_b} \frac{dV_b}{dT} \frac{dT}{dt} \quad (6.52)$$

$$C_j = g_j C_{sj0} \quad \text{at } t = 0 \quad \text{for } j = 1, \dots, n \quad (6.53)$$

6.7.2.2 Parameter Models

Listed below are models used to evaluate parameters required by the capture model. Some parameter evaluations are given in Appendix E, Appendix C lists the Fortran code, and listings of input files are included in Appendix K.

6.7.2.2.1 Reaction Rate Coefficients

Intrinsic reaction rate coefficients k_{ai} , and k_{aj} are modelled with an Arrhenius expression (Eqs. (6.54) and (6.55)). Values for these parameters were estimated from Uberoi (1990) in Appendix E ($A_i = A_j = 1.75 \times 10^6$ 1/(g silicate/cm³)/(cm² surface area/g silicate)/s, and $E_i = E_j = 156$ kJ/mol). The effectiveness factor was estimated to be near unity.

$$k_{ai} = A_i e^{-E_i/R_i T} \quad (6.54)$$

$$k_{aj} = A_j e^{-E_j/R_j T} \quad (6.55)$$

$$\eta_{ij} = 1. \quad \text{for } i, j = 1, \dots, n \quad (6.56)$$

Reaction coefficients for release of bound sodium, k_s , are modelled by Eq. (6.57). Parameters were estimated from constant heating rate data by Srinivasashar et al. (1990a) by the method discussed in Subsection 6.6.2.2 ($A_s = 3.59 \times 10^5 \text{ s}^{-1}$ for organically bound Na and $1.42 \times 10^5 \text{ s}^{-1}$ for NaCl, $E_s = 174. \text{ kJ/mol}$ for organically bound Na and $126. \text{ kJ/mol s}^{-1}$ for NaCl).

$$k_s = A_s e^{-E_s/R_s T} \quad (6.57)$$

6.7.2.2.2 Mass Transfer Coefficients

Mass transfer coefficients are modelled as diffusion to (or from) a sphere in a quiescent media. This assumption is justified since particle Reynolds numbers are expected to be low. The coefficient k_{mb} (from char to bulk gas) (cm/s) is modelled using Eq. (6.58) and multiplied by external surface area of char per unit volume gas in Eq. (6.59) (1/s).

$$k_{mb} = D_0/R \quad (6.58)$$

$$k_{mb} a_v = \frac{D_0 v}{R} \left(a_{v0} \frac{R^2}{R_0^3 T} \right) = a_{v0} \frac{D_0 v u}{D_0 T} \left(\frac{D_0}{R_0^2} \right) \quad (6.59)$$

The external char area per unit volume gas is given by Eq. (6.60) (cm^2/cm^3). Constant parameter a_{v0} is defined by Eq. (6.61) (K). Parameter v gives the temperature dependence of the diffusion coefficient with respect temperature T_0 , and u is the dimensionless char

$$a_v = \frac{(4\pi R^2)(\text{feedcoal}[\text{kg/hr}])}{(\rho_c \frac{4}{3} \pi R_0^3) 60(\text{feedair}[\text{slpm}])} \frac{298}{T} = \frac{a_{v0} R^2}{R_0^3 T} \quad (6.60)$$

$$a_{v0} = \frac{(\text{feedcoal})(298)}{\rho_0(20)(\text{feedair})} \quad (6.61)$$

radius R/R_0 . D_0 is a scaling diffusivity. Diffusivity of volatile in a char pore is D_{ab} ($2.418 \text{ cm}^2/\text{s}$ at 1273 K) and ϵ is char porosity assumed to be constant (0.3 unless otherwise specified).

$$D = [\epsilon^2 D_{ab}(T_0)] \left(\frac{T}{T_0} \right)^{1.63} \quad (6.62)$$

$$v(T) = \left(\frac{T}{T_0} \right)^{3/2} \quad (6.63)$$

Mass transfer coefficients from char matrix to included silicates, and from bulk gas to extraneous silicates are modelled using Eqs. (6.64) and (6.65) respectively. Coefficients are multiplied by respective external areas per unit volume. External areas of included silicates are expected to change at char burnout when one ash particle is formed.

$$k_{mi} = \frac{D_0 v}{R_i} \frac{4\pi R_i^2 f_i C_{sio}}{\frac{4}{3}\pi R_i^3 \rho_i} = \frac{3v f_i C_{sio} R_0^2}{\rho_i R_i^2} \left(\frac{D_0}{R_0^2} \right) \quad (6.64)$$

$$k_{mj} = \frac{D_{bo} v}{R_j} \frac{4\pi R_j^2 g_j C_{sjo}}{\frac{4}{3}\pi R_j^3 \rho_j} \frac{298}{T} = \frac{D_{bo}}{D_0} \frac{3v g_j C_{sjo} R_0^2}{\rho_j R_j^2} \frac{298}{T} \left(\frac{D_0}{R_0^2} \right) \quad (6.65)$$

6.7.2.2.3 Temperature

Gas temperature, T_g (K), was determined by fitting a four parameter model (Eq. (6.66)) to measured profiles, and combustor residence times (Appendix E). This fit was chosen simply because it follows the shape of measured profiles.

$$T_g(t) = a_1 (1 - e^{-a_2(t+a_4)}) e^{-a_3(t+a_4)} \quad (6.66)$$

The first parameter, a_1 , set the peak, a_2 determines the sharp rise, and the relatively slow drop after the peak is given by a_3 . An offset a_4 was used so temperature was not zero at time zero. Fit parameters for each burn are listed in Appendix E.

Residence time calculations accounted for geometry and temperature effects using the following assumptions: mass flow rate was constant and gas density varied as an ideal gas, fuel was completely consumed, temperatures were those measured by the thermocouple and were not corrected for radiation losses, temperatures varied linearly between measured points, and reduction of cross sectional area due to slagging was neglected. These residence times were used in Eq. (6.66).

Char particle temperature, $T_p(t)$ (K), was determined by Eq. (6.68) and initial condition (6.69). Char heat capacity

$$\frac{mC_p}{4\pi R^2} \frac{dT_p}{dt} + \frac{k}{R}(T_p - T_g) + \epsilon_p \sigma (T_p^4 - T_w^4) = k_c p_{O_2}^{1/2} (-\Delta H_{rxn}) \quad (6.67)$$

$$\frac{dT_p}{dt} = \frac{3}{\rho_c R C_p} \left(\frac{k}{R}(T_g - T_p) + \epsilon_p \sigma (T_w^4 - T_p^4) + k_c p_{O_2}^{1/2} (-\Delta H_{rxn}) \right) \quad (6.68)$$

$$T_p = T_g \quad \text{at } t = 0 \quad (6.69)$$

is given by $C_p = (4.03 + 0.00114T_p - 204000./T_p^2)/12$ (cal/g/K), radius is R (cm), and ρ_c is char density (1.4 g/cm³). Thermal conductivity of the gas film is k ($= 0.000207(T_m/1500.)^{1/2}$ (cal/s/cm/K)), ϵ_p is char emissivity (0.8), and σ is the Stefan-Boltzmann constant. Combustor wall temperature is $T_w (= 0.95T_g)$, and T_m is $(T_g + T_p)/2$. Oxidation rate coefficient is given by $k_c(T_p)$ (gC/s/cm²/atm^{1/2}), and p_{O_2} is oxygen partial pressure at the char surface (atm) discussed in more detail in the next section (Hurt and Mitchell (1992)). The heat of reaction is given by $\Delta H_{rxn} (= 25428. + 0.82T_p + 0.00033T_p^2 + 213000./T_p)/12$ (cal/g C)).

6.7.2.2.4 Char Radius

Char radius R was determined from burnout kinetics. R_{ac} , burnout rate, is given by Eq. (6.70). A_c (gC/s/cm²/atm^{1/2})

$$R_{ac} = A_c e^{-E_a/R_p T_p} p_{O_2}^{1/2} = k_c p_{O_2}^{1/2} \quad (6.70)$$

and E_{aC} (J/mol) are listed in input files in Appendix K (Hurt and Mitchell (1992), Hurt and Hardesty (1992)). Data acquired by Smith (1971) on bituminous coals was "compatible with the behavior of particles that shrink as they burn at constant density". Assuming constant ρ_c , R can be determined.

$$R_{ac} = \frac{D_{O_2}}{R} \frac{24}{R_g T_g} (p_{O_2} - p_{O_2,s}) = k_d (p_{O_2} - p_{O_2,s}) = k_c p_{O_2}^{1/2} \quad (6.71)$$

$$\frac{dm}{dt} = k_c 4\pi R^2 \left(\frac{(k_c^2 + 4k_d^2 p_{O_2})^{1/2} - k_c}{2k_d} \right) \quad (6.72)$$

$$\frac{4}{3} \pi \rho_c \frac{dR^3}{dt} = k_c 4\pi R^2 \left(\frac{(k_c^2 + 4k_d^2 p_{O_2})^{1/2} - k_c}{2k_d} \right) \quad (6.73)$$

$$\frac{dR}{dt} = \frac{k_c}{\rho_c} \left[\frac{\left[k_c^2 + 4k_d^2 p_{O_2} \right]^{1/2} - k_c}{2k_d} \right] \quad (6.74)$$

$$p_{O_2}(t=0) = \left(1 - \frac{w_{vol}}{w_{vol} + w_{fc}} \frac{1}{SR} \right) 0.21 \frac{p[\text{mmHg}]}{760} \quad (6.75)$$

$$p_{O_2}(t=t^*) = \left(1 - \frac{1}{SR} \right) 0.21 \frac{p[\text{mmHg}]}{760} \quad (6.76)$$

$$p_{O_2}(t) = p_{O_2}(0) - (p_{O_2}(0) - p_{O_2}(t^*)) \left(\frac{R_0^3 - R^3}{R_0^3 - R^{*3}} \right) \quad (6.77)$$

where $p_{O_2}(t)$ is the partial pressure of O_2 in the gas, and w_{vol} and w_{fc} are the weight fraction of volatile matter and fixed carbon respectively, and R^* is final char radius.

6.7.2.3 Results

Release parameters for organically bound Na (Na_{org}) and NaCl were extracted by the method discussed in Subsection 6.6.2.2. Figures 6.7-20 and 6.7-21 show good agreement between the first order kinetic model and data presented by Srinivasachar et al. (1990a). NaCl released between 1000 and 1600 K, and Na_{org} released between 1300 and 2000 K at a heating rate of 250 K/s

Figures 6.7-22 and 6.7-23 show results of the capture model and impactor data as a function of peak temperature for Beulah Lignite and Eagle Butte respectively. Data and model show variation in SR for samples acquired at the same peak temperature. Lines are least squares fits to the model (shown as filled squares for one line). Approximately half the bound Na was predicted to release due to char surface receding. This is in contrast to vaporization and diffusion within the char. Released Na can react with extraneous silicates, or diffuse back into the char to react with included silicates. If all silicates are included (0% extraneous) the model predicts a positive slope for f_{vNa} with increasing temperature. This is due to significant mass transfer resistance within the char, and shorter burnout times at higher temperatures. Reduction of silicate surface area at burnout due to coalescence essentially stops capture by included silicates. Less mass transfer resistance is encountered for extraneous silicates and faster reaction at higher temperatures results in a negative slope. Holding the total amount of silicates constant, capture of Na increases as the fraction of extraneous silicates increases. Extraneous silicates were assumed to be the largest in the silicate distributions (Sections 3 and 4).

FIGURE 6.7-20. - NaCl release.

FIGURE 6.7-21. - Na_(org) release.

FIGURE 6.7-22. - Capture model and impactor data for Beulah lignite.

FIGURE 6.7-23. - Capture model and impactor data for Eagle Butte.

Loy Yang, an Australian brown coal, has a low ash content (2 wt% DB) rich in Na and Cl. Figure 6.7-24 shows results for Loy Yang, and Loy Yang doped with kaolinite. Predictions for the raw coal give good results with respect to total capture, but the slope is slightly more negative than data indicate. Predictions for the doped coal showed more capture than was observed. Possible explanations are Cl inhibition of capture (Subsection 6.6.2.4), and fusion of kaolinite. Both mechanisms reduce capture and were not included in predictions. It should be noted that for burns of the doped coal, temperature profiles, which have a significant effect, were atypical.

In general, data for bituminous coals showed an *increase* of f_{vNa} as temperature increased. This is in contrast to the lower rank coals discussed above. Decrease with temperature was attributed to increased capture rate with temperature. For bituminous coals, such as Kentucky No. 11 (Figure 6.7-25), increase of f_{vNa} with temperature is attributed to silicates existing almost entirely as inclusions. Surface area of included silicates depends on char kinetics since at burnout inclusions coalesce. Kentucky No. 11 char was calculated to oxidize in a nearly kinetically limited mode. Capture by inclusions at higher temperatures is limited by shorter burnout times. Increasing char porosity decreases mass transfer resistance and increases capture by silicate inclusions.

FIGURE 6.7-24. - Capture model and impactor data for Loy Yang 2301.

FIGURE 6.7-25. - Capture model and impactor data for Kentucky No. 11

An empirical correlation predicted similar char oxidation kinetics for Illinois No. 6 and Kentucky No. 11 (Hurt and Mitchell (1992)). The correlation, which uses dry ash-free carbon content as the independent variable, predicts lower reactivity with increasing carbon content. Data for Illinois No. 6 shows an apparent increase of f_{vNa} with increasing temperature. Predictions, however show a decrease with temperature (Figure 6.7-26). This discrepancy could be due to a systematic error in calculation of coal feed rate and SR from flue gas composition and air feed rates for this coal. Ash trap sample carbon content was approximately 27% for all of Burn 47 (peak temperatures 1577 and 1641 K) (Boni, et al. (1991)). This indicates that coal feed rates were higher, and SR was lower than calculated based on complete combustion. Lower SR and significant unburned carbon suggest longer burnout times and greater capture than predicted by the model.

The complicated interaction of included silicate surface area, char oxidation kinetics, SR, and time-temperature history is reflected in results for Kentucky No. 9 (Figure 6.7-27). Model prediction (filled squares) agrees well with data. The variable behavior illustrates that peak gas temperature is not the only parameter dictating the fate of Na. Lower SR, for example, increases vapor Na concentration, and burnout times prolonging availability of included silicate surface area. Both increase total Na capture. Slower combustion rates, however also lower char temperatures which slows capture.

FIGURE 6.7-26. - Capture model and impactor data for Illinois No. 6

FIGURE 6.7-27. - Capture model and impactor data for Kentucky No. 9.

6.7.2.5 Discussion and Conclusions

Results for each coal illustrate the variable nature of Na behavior during pulverized coal combustion. Behavior of Na is complicated because it is a function of its original form, SR, char oxidation kinetics, and the quantity and mode of existence of silicates. No one variable was found to explain the entire range of behavior.

Kinetics of vaporization were found to have a significant influence on the rate and mechanism of vaporization, and extent of capture. In general sodium as NaCl (as was assumed for bituminous coals) vaporized and diffused out of the char early in combustion. Early release allowed for greater capture. Organically bound sodium (as was assumed for lower-rank coals) was found to vaporize at significantly higher temperatures. This linked a significant fraction of bound Na release to the char surface receding. Later release of organically bound sodium lowered the extent of capture.

Char oxidation kinetics were also found to dictate availability of included silicate surface area. Na capture by included silicates was essentially stopped at burnout due to coalescence. Faster burnout increased f_{vNa} by significantly reducing silicate area sooner in the combustion process.

The sum of mass transfer resistances for Na diffusing from the bulk flue gas phase to the char surface, through the char, and to included silicates was found to be significant. This was illustrated by model predictions of Beulah Lignite and Eagle Butte. Increasing the fraction of extraneous silicates shifted the slope of predicted f_{vNa} from positive to negative. This was due to lower mass transfer resistance and lower temperatures experienced by the extraneous silicates. Predictions and experimental results for doped Loy Yang suggest that including a silicate additive with the coal is a viable technique for reduction of vapor alkali.

Nomenclature for Section 6.7.2

a_i	($i=1,2,3,4$) temperature fit parameters (K, 1/s, 1/s, s).
A_i	preexponential for reaction of C_a with C_i ($1/(\text{cm}^2 \text{ silicate } i \text{ per g silicate } i) / (\text{g silicate } i \text{ per cm}^3 \text{ char}) / \text{s}$).
A_j	preexponential for reaction of C_b with C_j ($1/(\text{cm}^2 \text{ silicate } j \text{ per g silicate } j) / (\text{g silicate } j \text{ per cm}^3 \text{ flue}) / \text{s}$).
A_s	preexponential for release of C_s (1/s).
A_v	char surface area per volume flue ($\text{cm}^2 \text{ char} / (\text{cm}^3 \text{ flue})$).
A_{v0}	reference parameter for A_v (K).
C_a	concentration of volatile inside char ($\text{g/cm}^3 \text{ char}$).
C_b	concentration of volatile outside char ($\text{g/cm}^3 \text{ flue}$).
C_i	concentration of included silicate i ($\text{g } i / \text{cm}^3 \text{ char}$).
C_j	concentration of extraneous silicate j ($\text{g } j / \text{cm}^3 \text{ flue}$).
C_s	concentration of bound volatile ($\text{g/cm}^3 \text{ char}$).
C_{Si0}	initial concentration of included silicates ($\text{g/cm}^3 \text{ char}$).
C_{Sj0}	initial concentration of extraneous silicates ($\text{g/cm}^3 \text{ gas}$).

C_{s0}	initial concentration bound volatile (g/cm^3 char).
D	effective diffusivity of C_a inside char (cm^2/s).
D_{ab}	diffusivity of volatile in char pore (cm^2/s).
D_b	diffusivity of volatile in bulk flue gas phase (cm^2/s).
D_{b0}	diffusivity of volatile in bulk flue gas phase at reference temperature T_0 (cm^2/s).
D_0	scaling diffusivity (cm^2/s).
$E_{a\ i\ j}$	activation energy for $k_{a\ i\ j}$ (J/gmole).
E_{as}	activation energy for release of C_s (J/gmole).
E_c	activation energy for char oxidation (J/gmole).
f_i	fraction of inherent silicates that is species i .
f_{vNa}	fraction of sodium in the vapor.
g_i	fraction of extraneous silicates that is species j .
$k_{a\ i\ j}$	reaction rate coefficient (units of $A_{i\ j}$).
k_c	rate coefficient for char oxidation ($1/\text{s}/\text{cm}^2/\text{atm}^{1/2}$).
k_{mi}	mass transfer coefficient between C_a and C_i ($1/\text{s}$).
k_{mj}	mass transfer coefficient between C_b and C_j ($1/\text{s}$).
k_s	rate coefficient for release of C_s ($1/\text{s}$).
k_{mb}	mass transfer coefficient for transport of C_a from char to the bulk flue gas phase (cm/s).
m	char particle mass (g).
m	number of extraneous silicate species.
n	number of inherent silicate species.
PO_2	partial pressure of oxygen (atms).
PO_{2s}	partial pressure of oxygen at char surface (atms).
r	radial position inside spherical char particle (cm).
R	char particle radius (cm).
R_i	inherent silicate particle radius (cm).
R_j	extraneous silicate particle radius (cm).
R_0	initial char particle radius (cm).
R_*	final char particle radius (burnout complete) (cm).
S_i	surface area of inherent silicate i (cm^2/g).
S_j	surface area of extraneous silicate j (cm^2/g).
SR	stoichiometric ratio (air to coal).
t	temporal variable (s).
T	temperature (K).
T_0	reference temperature (K).
u	dimensionless char particle radius.
v	dimensionless temperature dependence of diffusivities.
V	char particle volume (cm^3 char).
V_b	bulk flue gas volume (cm^3 flue).
$\beta_{i\ j}$	stoichiometric factor ($\text{g silicate } i,j / \text{g Na}$).
ϵ	char porosity (cm^3 void) / (cm^3 char).
$\eta_{i\ j}$	effectiveness factor for silicate species i,j .
$\rho_{i\ j}$	silicate density (g/cm^3).
ρ_c	initial char particle density (g/cm^3).

τ dimensionless temporal variable.

feedair air feed rate into the combustor (slpm).

feedcoal coal feed rate into the combustor (kg/hr).

6.7.3 Alkali Study: Conclusions and Recommendations

Alkali behavior in pulverized coal combustion systems is affected by its original form, presence of silicates and other species, char oxidation kinetics, and its time-temperature history. Alkali originally present in silicates is not expected to vaporize (Boni et al. (1987)). Sodium existing as NaCl in the parent coal is expected to vaporize as NaCl_(v) (Yuh and Wolf (1984)), and at lower temperatures than organically bound sodium (Srinivasachar et al. (1990a)). Release of sodium at lower temperatures allows for longer interaction and greater capture of vapor sodium by silicates. Organically bound sodium release begins at temperatures lower than peak flame temperatures, but at temperatures high enough such that release can be linked to char oxidation. For low-rank coals, such as Beulah Lignite and Loy Yang, sodium bound to the organic matrix vaporizes as Na_(v), and vaporization follows first order kinetics.

This work and others have shown that silicates have a marked effect on alkali behavior. This effect is primarily through capture, although minerals also provide condensation sites for vapor alkali in cooler regions of combustion systems. Equilibrium calculations and experiments showed that sodium capture is greater for kaolinite than for silica. Addition of kaolinite to Loy Yang coal significantly reduced the fraction of sodium in the vapor. CCSEM results showed for combustion of Beulah Lignite that nepheline (Na₂O·Al₂O₃·2SiO₂) was one of the primary sodium silicates formed. Combustion of Loy Yang doped with kaolinite (Al₂O₃·2SiO₂) also formed nephelinite. These results suggest that vapor alkali (and fouling tendency) can be significantly reduced in combustion systems by a silicate additive. It is important, however that sufficient silicate be added such that viscosity of the additive is not significantly reduced as a result of alkali capture. Sticky alkali silicates could enhance fouling and slagging.

Equilibrium calculations by Wibberly and Wall (1982a) suggest that sodium silicate formation can occur under reducing conditions which exist inside burning chars. Some question remains if reduced sodium reacts with silicates as it diffuses out of the char, however no conclusive evidence exists to the contrary. Modelling efforts in this study assumed that reduced sodium could react with silicates as it diffused to the char surface. The capture mechanism for sodium released from the char may involve NaOH_(v) instead of NaCl_(v). This hypothesis is consistent with work showing sodium capture required the presence of water vapor (Bachovchin (1986), Punjak et al. (1989)). The reaction mechanism proposed in this study (reactions 6.78 and 6.79) is consistent with the mechanism proposed by Punjak et al. (1989) (reaction 6.80), and with experiments which showed less sodium silicate formation in the presence of chlorine. The higher capture rates predicted by reactions 6.78 and 6.79 were used in the model developed in Subsection 6.7. It is expected that capture rates

determined from experiments with $\text{NaCl}_{(v)}$ would be lower than practical systems if capture involves $\text{NaOH}_{(v)}$.

Chlorine has a significant effect on alkali behavior. Thermodynamic equilibrium calculations showed that MCl ($\text{M} = \text{Na}, \text{K}$) is stable above 1400 K (Subsection 6.6.1; also Wibberly and Wall (1982a), Scandrett and Clift (1990)). Chlorine inhibits alkali capture by silicates (Wibberly and Wall (1982a, 1982b), Lindner and Wall (1988, 1990)). Chlorine was also shown to be important in release of naturally involatile potassium from mineral matter (Gibb and Angus (1983)). This study showed evidence that both Na and Cl may be necessary to liberate mineral K, at least at lower temperatures. Potassium release also occurred only when sodium was captured, but the displacement was not a one-for-one ion exchange. The strong influence of chlorine on alkalis suggests that removal of chlorine from coal prior to reaching high temperatures of combustion systems is desirable with respect to both fouling and corrosion. Although chlorine can be removed from coal by prolonged aqueous washes, Hodges et al. (1983) showed that chlorine can be released from British coals at temperatures as low as 170°C as $\text{HCl}_{(v)}$.

Modelling suggests that the link between char oxidation kinetics and alkali behavior was twofold: 1) sodium bound to the organic matrix was released when the char surface recedes, and 2) at char burnout silicates coalesce reducing surface area available for capture. For highly reactive Beulah Lignite char, a significant fraction of the organically bound sodium was calculated to release as the char surface receded. In general, the less reactive bituminous coals showed less capture with increasing temperature. This was attributed to faster char oxidation and shorter burnout times at higher temperatures. Shorter burnout times reduced the time for coalescence of included silicates whose surface area would have otherwise been available for capture. The importance of char oxidation kinetics on alkali release and included silicate surface area availability, suggests that manipulation of char oxidation rates could increase capture by included silicates. Initially heating coal to high temperatures in an inert atmosphere prior to combustion would allow for release of sodium without significant reduction in char size. This would increase interaction time between vapor sodium and included silicates. In this study calculations used a single volume average char size. Future studies might include the effects of char size distributions on sodium behavior. Small char particles would be expected to reach burnout rapidly releasing all bound sodium, while larger particles would release sodium by both vaporization and char shrinkage.

Sodium capture was found to increase with temperature for low-rank coals.

Modelling suggested this was attributable to the presence of extraneous silicates. Relatively large mass transfer resistance reduced the temperature dependence for alkali reaction with included silicates. Less mass transfer resistance for extraneous silicates resulted in a more highly temperature dependent capture reaction. Increased capture with temperature was the result of increased reaction rates of sodium with extraneous silicates.

Atomically dispersed calcium in Beulah Lignite was found to contribute to formation of fly ash particles of two distinct compositions: CaO particles greater than 5 μm in size, and calcium silicate (consistent with gehlenite) found in particles from 0.65 to greater than 10 μm in size. This was attributed to coalescence of dispersed calcium as the char surface receded, and sloughing of large CaO particles from the char surface. Calcium was not enriched in the fume ($< 0.43 \mu\text{m}$) suggesting little or no calcium vaporized during combustion. This suggests problems associated with sodium could be reduced by removing ion exchangeable sodium by washing coal with an aqueous solution of calcium carbonate or calcium acetate. CaCl is not desirable due to possibility of increasing the chlorine content. Calcium, like sodium and potassium, can catalyze char gasification by steam (Hippo et al. (1979)), but is not expected to vaporize at char temperatures less than 2000 K (Graham et al. (1991)). Resulting calcium oxide can react with chloride (Pearce and Hill (1986)), and sulfur oxides reducing gaseous sulfur emissions.

Alkali behavior in coal combustion systems is complicated and affected by several variables. This study identified several important mechanisms governing alkali metal partitioning in a pulverized coal combustion environment. The mode of occurrence of alkali in the parent coal dictates its ability to vaporize, its release kinetics, and its state as it diffuses to the char surface. Vapor species such as chlorine, sulfur, moisture, and other metals influence alkali stability in the vapor, its reactivity, and its condensation characteristics. Silicates have a profound effect on alkali behavior primarily through capture. Char oxidation kinetics can influence alkali vaporization, and capture by affecting included silicate surface area. Char oxidation and capture is also influenced by the combustion stoichiometric ratio and the time-temperature history. This study suggests that a better understanding of physical, chemical, and kinetic parameters of silicate and coal char, in addition to alkali, is necessary to better understand alkali behavior in high temperature coal combustion systems.

6.8 Analysis - Iron Behavior

6.8.1 Background

It has long been known that iron content has a strong effect on the slagging and fouling characteristics of a coal. This effect can be attributed to the presence of molten extraneous pyrite and the formation of low melting point iron containing glasses. The behavior of the extraneous iron (primarily pyrites) under combustion conditions has been studied in detail by a number of investigator utilizing a wide range of techniques (Asaki et al, 1985, Groves et al, 1987, Huffman et al, Jorgensen, 1981, Thorpe et al, 1987, Srinivasachar et al, 1989, and others).

The iron contained within the carbon matrix has also been studied to determine its effect on the stickiness of the ash. 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 further determined that pyrite captured in a glass actually caused it to be come more sticky than an equal amount of iron oxide (Abbot et al, 1985). It is obvious then, that minimizing the amount of iron in the glassy phase should begin to minimize the slagging propensity of a coal.

Current control practices suggest that, by removing the ash extraneous to the coal, slagging may be minimized. However, some evidence would suggest that molten iron containing glass (from the inherent minerals) plays a more significant role than previously realized. Adams et al., 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. This work, utilizing a laboratory scale combustor and a number of analytical techniques, has provided some important insight on these points. The information obtained during this laboratory study was then used to develop a model to predict the partitioning of iron during pulverized coal combustion.

6.8.2 Iron-Silicate Interactions During Coal Combustion

Initial inspection of Mössbauer and CCSEM data for the Illinois No. 6 coal (see Table 6.8-1) presented a rather surprising discrepancy between the two techniques. According to the Mössbauer analysis approximately 84% of the iron was present 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 6.8-1). The first

TABLE 6.8-1. - 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 6.8-1. - Proposed iron-silicate interactions.

hypothesis was that the iron and silicates exist 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 proposed interaction mechanisms, a number of analytical tools were brought to bear on ash samples from two coals.

The first analytical tool used was an SEM coupled with an X-Ray detector. Approximately 11 particle agglomerates from an ash sample from a Beulah Lignite run 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 Figures 6.8-2 and 6.8-3 when compared with Table 6.8-2, indicate that iron oxide crystals were indeed present.

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 to 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.

FIGURE 6.8-2. - XRD spectrum from Illinois #6 ash trap sample.

FIGURE 6.8-3. - XRD spectrum from Illinois #6 ash trap sample.

TABLE 6.8-2. - Major XRD angles for magnetite and hematite

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

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 (see Figure 6.8-4)
- (2) the clusters of plate-like particles were predominantly Ca, S, Si (see Figure 6.8-5)
- (3) the large particles of beam stable material were almost completely pure Fe (see Figure 6.8-6)
- (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 (see Figures 6.8-7 and 6.8-8)
- (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.

FIGURE 6.8-4. - EDX spectrum of large glassy particles.

FIGURE 6.8-5. - EDX spectrum of plate-like particles.

FIGURE 6.8-6. - EDX spectrum of large beam-stable particles.

FIGURE 6.8-7. - EDX spectrum of needle-like particles in composite particles.

FIGURE 6.8-8. - EDX of glassy matrix of composite particles.

In addition, the particles mentioned in (3) above were assumed to have come from a discrete iron oxide particle as the typical dimensions were $1\text{ }\mu\text{m}$ by $0.3\text{ }\mu\text{m}$. 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. This behavior can be seen in Figures 6.8-9 through 6.8-16. In addition, this behavior was noted in both the study coals analyzed (Beulah Lignite and Illinois No. 6). This evidence suggests that the agglomeration mechanism was the dominant pathway for iron-silicate interactions within the char matrix. In addition, both the improbability (much less than 10%) of iron particles of these sizes impacting on the first impactor plate, 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.

V-663

FIGURE 6.8-9. - Ash agglomeration from Beulah Lignite, plate 1.

V-665

FIGURE 6.8-10. - Fe map, agglomerate in Figure 6.8-9.

V-664

FIGURE 6.8-11. - Si map, agglomerate in Figure 6.8-9.

V-662

FIGURE 6.8-12. - Agglomerate in Figure 6.8-9 under low magnification.

FIGURE 6.8-13. - Ash agglomerate from Illinois #6, plate 1.

V-661

FIGURE 6.8-14. - Fe map agglomerate in Figure 6.8-13.

V-660

FIGURE 6.8-15. - Si map, agglomerate in Figure 6.8-13.

FIGURE 6.8-16. - The agglomerate from Figure 6.8-13 under lower magnification.

6.9 Modeling of the Fate of Iron in Combustion-Derived Ash

Iron in coal has long been known to have a significant effect on the slagging propensity of that coal. This effect can, in part, be attributed to the fact that iron lowers the melting points of silicate melts and increases the melt's stickiness on steel substrates. In previous work (Boni, 1991) it was shown that agglomeration is the dominant mechanism for iron-silicate interaction during the combustion of pulverized coal. This mechanism has now been used to propose a model to predict the partitioning of the original iron between slag causing phases and crystalline phases.

6.9.1 Model Description

In the proposed model it is assumed that the inherent ash material does not interact appreciably with the extraneous ash material (i.e., no coagulation). Once this assumption has been made it is possible to model the partitioning of extraneous and inherent pyrite independently. The results of the independent modelling can then be combined to determine the overall partitioning of the original iron.

The inherent ash material is assumed to be initially 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. As the char is burned away inherent pyrrhotite and silicate particles are brought to the surface where they can either mix or oxidize (Figure 6.9-1). Iron oxide is formed when the pyrrhotite on the surface reacts with oxygen. The resulting oxide is either molten or solid, depending on the particle temperature. Glassy material is formed when molten silicates contact and mix with either molten iron oxide or pyrrhotite (Figure 6.9-2). By modelling the glass formation and the pyrrhotite oxidation, then, 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 and the solidification of the resulting oxide. The fraction of the original iron, inherent and extraneous, in slag causing phases (ϕ) can therefore be determined by combining the two independent models.

The important parameters for this model include the mass fractions of the inherent mineral matter (pyrite and silicates), the gas temperature profile, the stoichiometric ratio, and the silicate melting temperatures. Using these parameters, it is possible to determine the iron oxide formation rate, the iron glass formation rate, the char burnout rate, and the particle temperatures (char and extraneous pyrite).

FIGURE 6.9-1. - Pathway for ash movement to surface.

FIGURE 6.9-2. - Iron partitioning pathways.

6.9.2 Model Parameters

Before modeling the behavior of the inherent mineral matter, it was necessary to determine several important parameters. These parameters include the mass fractions of the inherent mineral matter, the mass mean sizes of the inherent material, the percent carbon in the coal, the silicate melting temperatures, and the percent volatile matter.

The mass fractions and mass mean sizes of the inherent material was determined from CCSEM (Computer Controlled Scanning Electron Microscopy) analysis, performed at the University of Kentucky, of both the original coal and the combusted ash. From CCSEM of the original coal it was possible to estimate the mass mean sizes of the inherent mineral matter. The mass fractions of inherent material was estimated from CCSEM analysis of the combusted ash. It was assumed from the previously mentioned work (Boni, 1991) that 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 iron, 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). In addition, as the CCSEM analysis was only performed on the ash from plate 1 and the cup of the impactor ($>9\mu\text{m}$), it was assumed that the remaining ash ($<9\mu\text{m}$) was initially inherent. The average fraction of both silicate and iron mass captured in the analyzed fraction was determined from previous experimental data. The results of these calculations can be seen in Table 6.9-1.

The additional coal derived parameters; the percent carbon and the percent volatile matter, were obtained from coal analysis performed by Foster Wheeler Corporation. The silicate melting temperatures utilized were as shown in Table 6.9-2. The quartz and kaolinite melting temperatures were those for the pure species. The illite and "mixed silicate" melting temperatures were estimated from equilibrium diagrams ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$, Slag Atlas, 1989). Experimental parameters used in the model, specifically the stoichiometric ratio and the gas temperature profile, were determined as part of the experimental procedure.

TABLE 6.9-1. - Model input parameters

Coal	Illinois #6	Kentucky #11	Kentucky #9	Upper Freeport	Beulah Lignite	Eagle Butte
g ash/g coal	0.086	0.203	0.143	0.232	0.096	0.048
MF sil. in ash	0.633	0.704	0.808	0.788	0.713	0.879
MF pyr. in ash	0.2800	0.2400	0.1600	0.1800	0.2600	0.0400
MF ext. sil [*]	0.3687	0.1880	0.2230	0.2260	0.2840	0.3330
MF ext. pyr ^b	0.4300	0.3100	0.3540	0.1600	0.4200	0.2500
MF ash > 9 μm	0.8730	0.9000	0.8350	0.9200	0.6880	0.8095
MF iron > 9 μm	0.9240	0.9360	0.9070	0.9050	0.7925	0.6590
Inh. sil. ^{**}	0.0369	0.1187	0.0940	0.1448	0.0551	0.0308
Inh. pyr. ^{**}	0.0145	0.0346	0.0155	0.0357	0.0167	0.0016
Ext. pyr. ^{**}	0.0096	0.0141	0.0073	0.0060	0.0083	0.0003
Frac. C (ash and H ₂ O free)	0.775	0.768	0.775	0.847	0.686	0.718
Frac. volatiles (as received)	0.359	0.338	0.345	0.240	0.293	0.338
Fraction silicates as quartz [*]	0.370	0.280	0.160	0.140	0.210	0.550
Fraction silicates as Kaolinite [*]	0.110	0.130	0.080	0.100	0.530	0.180
Fraction silicates as Illite [*]	0.190	0.240	0.310	0.480	0.020	0.030
Fraction silicates as "Mixed Si" [*]	0.330	0.350	0.450	0.280	0.240	0.240
[*] From CCSEM. ^{**} g/g coal (from CCSEM and includes ash < 9 μm).						

TABLE 6.9-2. - Silicate melting temperatures (Slag Atlas, 1981)

Silicate	Melting Temperature (K)
Illite	1625
Kaolinite	2083
"Mixed"	1258
Quartz	1983

6.9.3 Char Burnout

The char burnout relation used, Eq. (6.81), was that presented by Hurt and Mitchell

$$\frac{d(\text{CHAR})}{dt} = -k_c \exp \left[\frac{-E_c}{RT_p} \right] SA_{\text{char}} (P_{O_{2s}})^{1/2} \quad (6.81)$$

(1992) (and is the same relation described previously, in Subsection 6.7.2.2.4). According to this empirical study, the char burnout is a function of the char external surface area (SA_{char}) and the char particle temperature (T_p). The burnout rate was further assumed to go as the square root of the surface oxygen partial pressure ($P_{O_{2s}}$). Finally, the rate constants were determined to be a function of the coal carbon content as shown in Eq. (6.82) and (6.83) (Hurt et al, 1992).

$$E_c = -5.945 + 0.355(\%C) \quad (6.82)$$

$$\ln k_c = (2.80 + 0.0758(\%C)) - \left[\frac{E_c}{1750 R} \right] \quad (6.83)$$

In the partitioning model the combustion product is assumed to be CO. The CO is then oxidized to CO₂ in the bulk gas phase according to Eq. (6.84). The

reaction rates, r_f and r_b , shown in Eqs. (6.85) and (6.86) are those presented by Dryer et al. (1973) and Westbrook et al (1981) respectively. The species concentrations are determined from the number of moles of each species in the system and the gas volume, determined from Eq. (6.87). Mole balances for O₂, CO, CO₂ are shown in Eqs. (6.88) through (6.90). Finally, the surface partial pressure of oxygen is determined by assuming a steady state between oxygen transport and consumption (see Eq. (6.91)).

$$r_f = 3.8 \times 10^{14} \exp \left[\frac{-E_{\text{CO}}}{R T_g} \right] [\text{CO}] [\text{H}_2\text{O}]^{1/4} [\text{O}_2]^{1/2} \quad (6.85)$$

$$r_b = 1 \times 10^{11} \exp \left[\frac{-E_{\text{CO}}}{R T_g} \right] [\text{CO}_2] \quad (6.86)$$

$$V_g = \frac{n_t R T_g}{p} \quad (6.87)$$

$$\frac{d\{\text{O}_2\}}{dt} = \frac{1}{24} \frac{d(\text{CHAR})}{dt} + \frac{1}{2}(r_b - r_f) \quad (6.88)$$

$$\frac{d\{\text{CO}\}}{dt} = -\frac{1}{12} \frac{d(\text{CHAR})}{dt} + (r_b - r_f) \quad (6.89)$$

$$\frac{d\{\text{CO}_2\}}{dt} = r_f - r_b \quad (6.90)$$

$$\left[\frac{D}{r_c} \right] \left[\frac{P_{O_2} - P_{O_{2s}}}{R T_g} \right] = \frac{-k_c}{24} \exp \left[\frac{-E_c}{R T_p} \right] (P_{O_{2s}})^{1/2} \quad (6.91)$$

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.

6.9.4 Glass Formation

The proposed glass formation rate (Eq. (6.92)) is based on a mixing rate and the probability of contact between the necessary species. The mixing rate component (M_g) contains the only fit parameters in the model. The first fit parameter is the amount of silicate consumed during glass formation (see Eq. (6.93) and (6.94)). The second fit parameter is the rate constant, k_g , for mixing between molten iron and silicate species (Eq. (6.95)). Finally, the temperature dependence of the mixing rate (E_g) was assumed to be that of iron diffusing into a silicate melt (Turkdogan, 1983).

$$\frac{d(G)}{dt} = k_g \exp \left[\frac{-E_g}{R T_p} \right] (\text{Sil}) X_g \quad (6.92)$$

$$M_g = k_g \exp \left[\frac{-E_g}{T_p} \right] \quad (6.95)$$

The next major component of the glass formation rate is the probability that the silicate species contact iron species as opposed to any other species. This probability was written as the total cross-sectional area of silicates on the surface (Eq. (6.96)) times the relative cross-sectional area of iron (X_g , Eq. (6.97)).

$$CSA_{sil} = (Sil) \frac{3}{4 r_{sil} \rho_{sil}} \quad (6.96)$$

$$X_g = \frac{CSA_{molten}}{SA_{char} - CSA_{molten}} \quad (6.97)$$

For example, in Figure 6.9-3 the probability that the silicates would contact an iron species is fairly high as there is primarily iron and silicates on the surface. As the other species (glass and solid iron oxide) begin to predominate on the surface, Figure 6.9-4, the probability of silicates contacting the iron is lower as the other species may 'get in the way'.

FIGURE 6.9-3. - High probability of contact.

FIGURE 6.9-4. - Low probability of contact.

The mass of silicates on the surface, as discussed above, is a very important parameter. For the purpose of this model, the surface of the char is treated as a batch reactor (Eq. (6.98)). The mass of silicates that have come into the 'reactor',

$$(\text{Sil}) = \{(\text{CHAR})_0 - (\text{CHAR})\} \text{MF}_{\text{sil}} - (G) \left[\frac{y}{y+1} \right] \quad (6.98)$$

then, 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. However, 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.

6.9.5 Iron Oxide Formation

The iron oxide reaction pathway utilized by this model was that presented by Srinivasachar et al. (1989). The pathway, Figure 6.9-5, was used as described for the extraneous pyrite with a few simplifications. For the inherent pyrite, however, the mechanism was somewhat modified. 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. If the particle temperature is less than the pyrrhotite melting point (1356 K) the exposed inherent pyrrhotite oxidizes according to Eq. (6.99), where SA_{pyr} is defined by Eq. (6.100). The parameters, E_p and k_p , were $5 \times 10^7 \text{ ms}^{-1}$ and 150 kJ mole^{-1} as

$$\frac{d(\text{Fe}_3\text{O}_4)}{dt} = k_p \exp \left[\frac{-E_p}{RT_p} \right] SA_{\text{pyr}} \left[\frac{P_{\text{O}_{2s}}}{RT_p} \right] \quad (6.99)$$

$$SA_{\text{pyr}} = (\text{Fe}_{0.877}\text{S}) \frac{3}{r_{\text{pyr}} \rho_{\text{pyr}}} \quad (6.100)$$

proposed by Srinivasachar (1989) from work by Asaki et al. (1985). The extraneous pyrrhotite also oxidizes according to Eq. (6.99). However, in this case SA_{pyr} is the surface area of the extraneous pyrite, the $P_{\text{O}_{2s}}$ is that for the surface of the pyrite.

Reaction Pathway for Inherent Pyrite

FIGURE 6.9-5. - Oxidation pathways for inherent and extraneous pyrite.

For temperatures greater than the melting point, oxidation of the melted pyrrhotite is assumed to be limited by the transport of oxygen to the surface as suggested by several investigators (Srinivasachar, 1989, Asaki et al., 1985, Jorgensen, 1981a, 1981b). The extraneous pyrite, then, should oxidize according to Eq. (6.101), where k_m depends on the extraneous pyrite size (Eq. (6.102)). This k_m dependence assumes that the particle is falling at the same rate as the gas flow, and thus 'sees' a stagnant fluid. The numerical part of Eq. (6.102) is the stoichiometric conversion from moles O_2 consumed to mass Fe_3O_4 formed. For an inherent particle, however, the mass transfer coefficient (k_m) would depend on the melt particle size rather than the char particle size. This size dependence is due to the assumption that the entire pyrite particle is inside the diffusion film for the char. For this reason, the transport of oxygen to the inherent particle is assumed to depend on PO_{2s} rather than PO_2 .

$$\frac{d(Fe_3O_4)}{dt} = k_m PO_2 \quad (6.101)$$

$$k_m = \frac{63.784 D}{r_{extpyr} T_g R} \quad (6.102)$$

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

The final important iron oxidation parameter is the amount of pyrrhotite, ($\text{Fe}_{0.877}\text{S}$), on the surface. In this case the surface is, again, treated as a batch reactor (Eq. (6.103)).

$$(\text{Fe}_{0.877}\text{S}) = \{(\text{CHAR})_0 - (\text{CHAR})\} \text{MF}_{\text{pyr}} - \frac{(G)}{1+y} - \frac{(\text{Fe}_3\text{O}_4)}{0.827} \quad (6.103)$$

The mass of pyrrhotite on the surface depends on the amount of carbon burned away, the amount of iron oxide formed, and the amount of glass formed from pyrrhotite capture. 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 1870 K from the system while allowing iron oxide formed at temperatures greater than 1870 K to remain in the system until the temperature reaches 1600 K. In this manner molten iron oxide is available for capture by the silicates. The solid oxide, on the other hand, is treated as a final product (this assumes that the iron oxide solid does not melt).

6.9.6 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 (Eq. (6.104)) and the extraneous pyrite (Eq. (6.105)). Each energy balance consisted of a conduction term, a radiation term, and a reaction term.

$$\frac{dT_p}{dt} = \frac{SA_{\text{char}}(h(T_g - T_p) + \sigma\epsilon(T_w^4 - T_p^4)) + \frac{d(\text{CHAR})}{dt}\Delta H_c}{C_p(\text{CHAR})} \quad (6.104)$$

$$\frac{dT_{\text{pyr}}}{dt} = \frac{SA_{\text{extpyr}}(h(T_g - T_{\text{pyr}}) + \sigma\epsilon(T_w^4 - T_{\text{pyr}}^4)) + \frac{d(\text{Fe}_3\text{O}_2)}{dt}\Delta H_r}{C_{p_{\text{pyr}}}(\text{Fe}_{0.877}\text{S})_{\text{ext}}} \quad (6.105)$$

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 and a wall temperature (T_w) of 98% of the gas temperature. The final energy term for the char energy balance, heat released by combustion of the char, was based on the assumption that CO is the primary reaction product. Ash and char heat capacities were calculated from data presented in the *Coal Conversion Systems Technical Data Book* (1983). For the extraneous pyrite energy balance 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).

6.9.7 Model Results

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 6.9-3, include the peak gas temperature (and the gas temperature profile), the coal composition, and the stoichiometric ratio. The experiments, and therefore simulations, performed to date include temperature variations and coal composition variations. The stoichiometric ratio, on the other hand, was always

TABLE 6.9-3. - Experimental parameters

Run	Coal	Feedrate (kg/hr)	Stoichiometric Ratio	Peak Gas Temperature
21	Illinois 6	1.7	1.27	1362
47b	Illinois 6	1.3	1.30	1304
67	Kentucky 9	1.7	1.30	1226
27	Kentucky 11	1.7	1.25	1320
56c	Kentucky 11	1.3	1.25	1240
56f	Kentucky 11	2.1	1.20	1429
22	Beulah Lignite	2.4	1.32	1294
48b	Beulah Lignite	1.6	1.26	1160
48f	Beulah Lignite	2.6	1.37	1245
32	Upper Freeport	1.7	1.23	1347
35	Upper Freeport	1.7	1.22	1300
23	Eagle Butte	2.3	1.26	1220
61	Eagle Butte	2.1	1.33	1193

approximately 1.25. The previously mentioned fit parameters, k_g and y , were determined to have values of approximately 6,000 (g glass s⁻¹ cm⁻²) and 3 respectively.

A comparison of the predicted versus measured partitioning of iron into the glassy phase, ϕ_g , (Figure 6.9-6) shows that the model agrees reasonably well with the data. The experimental error was based on the fraction of iron not captured on plate 1 and the cup (and therefore not measured with Mössbauer), and the error in the Mössbauer analysis. The fraction of iron in the glassy phase (ϕ_g) seems to increase slightly with increasing temperature (see Table 6.9-4). This could be due to the increase in the amount of iron (specifically as oxide) available for capture at the higher temperatures. The predicted temperatures, phase partitioning, char behavior, and slag causing phase partitioning can be seen in Figures 6.9-7 through 6.9-10.

FIGURE 6.9-6. - Comparison of predicted and measured fraction iron as glass.

TABLE 6.9-4. - Simulation results

Run	Coal	ϕ_g (meas.)	ϕ_g (pred.)	Peak Char Temperature (K)	Peak Pyrite Temperature (K)
21	Illinois 6	0.160	0.160	1794	2029
47b	Illinois 6	0.180	0.145	1740	1998
67	Kentucky 9	0.190	0.190	1715	1970
27	Kentucky 11	0.260	0.308	1802	1960
56c	Kentucky 11	0.230	0.254	1745	2023
56f	Kentucky 11	0.335	0.514	2032	2012
22	Beulah Lignite	0.280	0.404	1983	1867
48b	Beulah Lignite	0.370	0.376	1942	1828
48f	Beulah Lignite	0.380	0.474	2113	1916
32	Upper Freeport	0.300	0.484	1757	2068
35	Upper Freeport	0.400	0.349	1645	2098
23	Eagle Butte	0.540	0.460	2002	1947
61	Eagle Butte	0.720	0.532	2089	1937

FIGURE 6.9-7. - Predicted temperature profiles.

FIGURE 6.9-8. - Iron partitioning as a function of residence time.

FIGURE 6.9-9. - Char behavior as a function of residence time.

FIGURE 6.9-10. - Fraction iron in slag-causing phases as a function of time.

6.9.8 Future Work

The modelling done to date has explored the effect of temperature and coal composition on the partitioning of iron. However, one major parameter, the stoichiometric ratio, has not yet been sufficiently explored with respect to the iron partitioning. Future work, therefore, will involve experiments with one coal (specifically the Kentucky 11 coal) under various stoichiometric ratios. The experimental results could then be used to test the validity of the partitioning model and to define any necessary modifications.

6.10 Variable Definitions

Variable	Definition
(CHAR)	Mass of Char (g)
(CHAR) ₀	Initial Mass of Char (g)
C _p	Mean Char Heat Capacity (cal g ⁻¹ K ⁻¹)
C _{p 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 _{pyr}	Total Cross-sectional Area Pyrrhotite (cm ²)
CSA _{molten}	Total Cross-Sectional Area Molten Iron Compounds (cm ²)
D	Gas Phase Diffusivity (cm ² s ⁻¹)
E _c	Char Oxidation Activation Energy (kcal mole ⁻¹)
E _k	Mixing Rate Temperature Dependence (K)
E _p	Iron Oxidation Activation Energy (kcal mole ⁻¹)
(Fe ₃ O ₄)	Mass 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) _{ex}	Mass of Extraneous Fe _{0.877} S Particle (g)
(G)	Mass Glass on Char Surface (g)
[H ₂ O]	Concentration Water (mole cm ⁻³)
k _c	Char Oxidation Rate Constant (gC s ⁻¹ cm ⁻² atm ^{-1/2})
k _k	Glass Formation Rate Constant (gG s ⁻¹ cm ⁻²)
k _p	Iron Oxidation Rate Constant (cm s ⁻¹)
M _k	Silicate-Iron Mixing Rate Constant (g cm ⁻²)
MF _{pyr}	Mass Fraction Inherent Pyrite in Coal
MF _{sil}	Mass Fraction Inherent Silicate in Coal

Variable Definitions (cont'd)

Variable	Definition
n_t	Total Number Gaseous Moles in System
P_{O_2}	Oxygen Partial Pressure in Bulk Phase (atm)
$P_{O_{2s}}$	Oxygen Partial Pressure on Surface (atm)
P	Total System Pressure (atm)
R	Gas Constant
r_b	Rate of CO_2 Reduction (mole $cm^{-3} s^{-1}$)
r_c	Radius of Char (cm)
r_f	Rate of CO Oxidation (mole $cm^{-3} s^{-1}$)
r_{pyr}	Mass Mean Radius Inherent Pyrite (cm)
r_{sil}	Mass Mean Radius Inherent Silicate (cm)
r_{extpyr}	Mass Mean Radius Extraneous Pyrite (cm)
SA_{char}	External Surface Area Char (cm^2)
SA_{extpyr}	External Surface Area Extraneous Pyrite (cm^2)
SA_{pyr}	External Surface Area Char (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)
ΔH_c	Heat of Combustion for Char (cal g^{-1})
ΔH_r	Heat of Reaction for Pyrrhotite (cal g^{-1})
ϵ	Emissivity
σ	Stefan-Boltzmann Constant (cal $sec^{-1} cm^{-2} K^{-4}$)
ρ_{sil}	Density of Silicates (g cm^{-3})
ρ_{pyr}	Density of Pyrite (g cm^{-3})

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SECTION 7

TASKS 7 AND 8

**IDEALIZED COMBUSTION DETERMINATION OF ASH PARTICLE FORMATION
AND SURFACE STICKINESS (PSIT)**

AND

**DEVELOPMENT OF AN ENGINEERING MODEL FOR THE PREDICTION OF ASH
PARTICLE SIZE AND CHEMICAL COMPOSITION DISTRIBUTIONS (PSIT)**

7. IDEALIZED COMBUSTION DETERMINATION OF ASH PARTICLE FORMATION AND SURFACE STICKINESS (PSIT)

AND

DEVELOPMENT OF AN ENGINEERING MODEL FOR THE PREDICTION OF ASH PARTICLE SIZE AND CHEMICAL COMPOSITION DISTRIBUTIONS (PSIT)

The PSI Technology Co. (PSIT) portion of this program was broadly defined as a study to identify the most important factors determining the characteristics of fly ash and ash deposits. The study was composed of two tasks, with Task 7 defined as an experimental task and Task 8 as a modeling task. Three primary objectives were defined by PSIT at the beginning of this program: 1) the identification of the most important factors governing the ash particle size distribution; 2) the identification of the most important factors determining the distribution of ash particle chemical compositions; and 3) the quantification of the stickiness of individual ash particles. Several specific studies were carried out to meet these objectives. As discussed in other sections of this report, the work was further subdivided into Phase I - parent or "raw" coals, and Phase II - beneficiated and blended coals. These specific studies and the associated program Phase are listed below.

- study of key mineral interactions for bituminous, low-rank, beneficiated, and blended coals (Phase I, II)
- study of mineral fragmentation (Phase I)
- measurement of excluded pyrite transformations (Phase I)
- examination of extraneous clay mineral transformations (illite, kaolinite, montmorillonite, nepheline) (Phase I, II)
- assessment of the importance of combustion scale (reactor size) in determining ash particle size and particle chemical composition distributions, through comparison of results with the University of Arizona (UA) and joint tests conducted at UA and the State Electricity Commission of Victoria (SECV) (Phase I, II)
- study of the partitioning of ash into submicron ("fume") and super-micron fractions (Phase I); exploration of the impacts of beneficiation on partitioning (Phase II)
- preliminary exploration of the effects of reducing conditions (i.e., variable combustion stoichiometry) on ash particle chemical composition distributions (Phase II)

- preliminary exploration of trace metal transformations for parent and cleaned coals, focusing on Cr (Phase II)
- detailed study of sodium evolution (Phase I), including in-situ measurements of vapor phase molecular NaCl in the post (coal) combustion gases via LIPF (Phase I)
- study of ash particle stickiness and the role of particle viscosity in deposit initiation (Phase I, II)
- development of pyrite transformation kinetics model (Phase I)
- equilibrium modeling of ash thermochemistry (Phase I)
- modeling of homogeneous vapor phase sodium kinetics (Phase I)
- development of an overall, fundamentally-based "Engineering Model" to predict ash particle size and particle chemical composition *distributions* (Phase II).

Phase I results were described in detail in the Phase I Final Report (Boni et al., 1990). In this section of the Final Report, Phase I results are summarized where appropriate; emphasis is placed on those activities occurring during the final 2-1/2 years (Phase II) of this program.

7.1 Background

As described in previous reports and many papers in the open literature (e.g., Bryers, 1987), it is individual ash particles that are responsible for the initiation of deposition in utility boilers. That is, it is the size and chemical composition of *individual ash particles* that determines whether a particle will impact and stick to a heat transfer surface. Conventional approaches for predicting the magnitude of deposition rely on empirical indices that use the bulk ash composition of the coal. Because these indices do not account for the wide distribution of particle sizes and particle chemical compositions existing in fly ash, they are inaccurate and often unreliable indicators when used beyond the design range of boiler and coal types. With more utilities considering fuel switching and blending, particularly in response to the SO₂ control provisions of the 1990 Clean Air Act Amendments, improved predictors for deposition are essential.

The importance of ash particle size distributions to deposition is apparent. Impaction driven by inertial forces, thermophoresis, and eddy diffusion are the major transport mechanisms driving ash particles from the hot gas toward cooler heat transfer surfaces; each is particle size dependent. The ash particle *composition* distribution is equally important to the deposition process, however. This perhaps can best be illustrated by an example. Consider the base to acid ratio, one of the indices used to characterize deposition and defined

as $\{\text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MgO} + \text{CaO}\} / \{\text{SiO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3\}$. A value of 0.5 is generally considered the maximum allowable value for dry bottom units (Winegartner, 1974). For the Illinois #6 bituminous coal examined in Phase I of this program, a value slightly less than 0.5 is obtained using the ash composition in Table 3.15. If the distribution of ash particle compositions measured experimentally and reported in Boni et.al. 1990, is used, however, a significant mass of ash particles can be shown to lie above the 0.5 threshold value (Figure 7.1-1). Thus, while the bulk composition is "acceptable," approximately 30% of the ash would be deemed unacceptable if the *distribution* of compositions were considered. It is therefore critical that the distribution of particle compositions be understood and predictable, particularly as a function of ash particle size.

Much recent work has described the factors affecting ash particle size distributions in detail. Good summaries are contained in recent Engineering Foundation conference proceedings (Benson, Ed., 1991; Bryers and Vorres, Eds., 1990) a special issue of *Progress in Energy and Combustion Science* (16{4}, 1990), several *Proc. of the International Symposia on Combustion* (e.g., Wall, 1992; Flagan, 1979; Neville and Sarofim, 1983), Raask (1985), and a review by Helble et.al. (1990a). Many other reviews and individual papers address this topic and are cited in the reference lists of the aforementioned publications.

FIGURE 7.1-1. - Mass probability distribution of base/acid ratios for distribution of ash particle chemical compositions measured in a bench-scale combustion experiment at PSIT. Model curve represents results of Engineering Model calculation (see Subsection 7.9 text).

In all of this work, however, a focus on individual mineral interactions has been missing, as has a detailed description of particle stickiness and an overall model describing these processes. These issues have been addressed in great detail by the investigators of this program during Phases I and II. This was accomplished through a combination of fundamental laboratory scale experiments, pilot scale experiments at SECV, and fundamental modeling. Details of specific PSIT activities in these areas are discussed in the following sections.

7.2 Experimental Approach

7.2.1 Combustion and Particle Collection Systems

PSIT combustion experiments were conducted in the resistance-heated laminar flow drop tube reactor shown in Figure 7.2-1. The body of the furnace, consisting of the drop-tube section, was an Applied Test Systems Series 3420 three-zone furnace. The maximum operating (wall) temperature of this system was 1540°C. For most of the experiments described herein, a methane-fired swirl stabilized reactor assembly was mounted at the inlet of the 8.6 cm (3-3/8 in.) I.D., 1.3m (51 in.) long drop-tube section. This provided increased residence time for complete combustion of the large particles present in utility

FIGURE 7.2-1. - PSIT laboratory reactor.

grind coal samples, and simulated on a small scale particle concentrations present in an actual combustor. In the pre-fired section, methane constituted 75 to 80% of the total energy input, with coal injected slightly downstream of the methane providing the remainder. Samples of pulverized coal, typically ground to 70% less than 200 mesh ($74\ \mu\text{m}$), were mechanically fed to the swirl stabilized reactor at feed rates of 0.2 to 2.5 g/min, utilizing the feeder system depicted in Figure 7.2-2. Coal was loaded into three horizontally-mounted 5.1 cm (2 in.) long x 12.7 mm (0.5 in.) I.D. teflon tubes, stacked vertically. Coal particles were injected into a downward flowing airstream by a Sage Instruments Model 351 syringe pump that pushed a rotating plastic paddle assembly, preventing agglomeration in the feed tube. Direct mechanical feeding was essential in these experiments to avoid the coal particle size segregation which occurs in fluidized or entrained bed feeders. For feed rates of 2.5 to 5 gm/min, an auger screw feeder was used.

Gas flowrates to the system varied, depending upon desired residence times, oxygen levels, and amount of gas preheating. For the most common condition of 3s residence time, system flows were 1.8 slpm of methane, 6.2 slpm of coal feeder air, and 20.3 slpm of oxygen/nitrogen mixture, giving a total flow of 28.3 slpm. Of this, 8.3 slpm were extracted by the collection probe, to which 20 slpm of quench nitrogen were added. Oxygen/nitrogen mixtures were injected through a separate port at the inlet to the swirl stabilized section. Particle ignition occurred near the exit of the methane-air flame. Post-methane-flame oxygen levels in this region were maintained at 3, 7, or 21%, corresponding to an air/fuel ratio of 1.2 to 10 (also dependent upon particle feed rate).

FIGURE 7.2-2. - Schematic diagram of feeder designed to feed 70% < 200 mesh grind uniformly.

At the exit of the swirl-stabilized section, particles entered the isothermal zone of the drop tube furnace. Gas temperatures in this region were maintained at 1500 to 1700 K, depending upon the goal of the experiment. Particle residence times within the 1.3m isothermal section were approximately 3s at 1700 K, permitting complete burnout of the largest particles to occur. Selected Phase I experiments were also conducted at the MIT drop tube furnace facility described in Section 5 of this report. Selected Phase II experiments were conducted at the University of Arizona facility described in Section 6 of this report.

Upon completion of combustion, ash particles were sampled by one of the following two techniques:

1. Isokinetic sampling through a 19 mm I.D., 51 mm O.D., 61 cm long stainless steel water-cooled nitrogen-quenched sampling probe. The top 25 mm of the probe was tapered to a "point", from an O.D. of 51 mm at the base to an O.D. of 19 mm at the tip, to minimize perturbations in the reactor gas flow. Approximately 10 to 20% of the total ash particles were extracted from the well-dispersed flow volume in a typical experiment. Calculated particle quench rates were 10^4 K/s over the length of the probe. Higher rates are expected at the tip. In experiments conducted at the MIT facility, all of the ash particles generated during combustion were collected (non-isokinetic sampling). At the exit of the probe, all particles were either (a) deposited on the greased (Fomblin YVAC 3) stages of a Pollution Control Systems Corporation seven-stage cascade impactor, with backup Poretics polymer-based final filter, for on-line size classification, or (b) collected on a total filter for subsequent size and chemical composition measurement by CCSEM. In both cases, the duration of a typical experiment was 20 to 30 min of coal feeding.
2. Deposition of a small portion of the ash particles on a "stickiness" probe, depicted schematically in Figure 7.2-3. In this probe, narrow diameter mullite tubes (1.5 to 3 mm) were placed in a conical ceramic converging section oriented perpendicular to the bulk gas flow. Tube sizes were chosen so that a well defined fraction of particles would impact the tube surface. For appropriately large particle sizes (e.g., the synthetic glass experiments to be discussed later), the impaction efficiency was 100%. Sticky supermicron particles were defined as those adhering to the tube after impaction. The velocity of the particles at the tube surface was varied from 1 to 5 m/s by changing the location of the tubes within the converging section. Temperature profiles within the converging section as a function of location and furnace gas temperature are given in Figure 7.2-4. Note that these temperatures were made with an unshielded thermocouple and were not radiation-corrected. An exception is the curve labeled "suc pyr" for which a suction pyrometer was used to measure temperatures.

7.2.2 Particle Size and Composition Distribution Analysis

Particle size distributions were measured by one of four techniques. When chemical composition and particle size of ash particles $> 1 \mu\text{m}$ in size were required, ash particle microscopy (CCSEM). When size distributions only were required, ash samples were

C-2565a

FIGURE 7.2-3. - Particle stickiness (adhesion efficiency) probe. Drawing not to scale; dimensions as indicated

C-2747a

FIGURE 7.2-4. - Furnace - probe temperatures.

samples were collected on a filter and analyzed by computer controlled scanning electron analyzed with a Malvern Instruments light scattering device. When information on the amount of submicron aerosol was needed, a Pollution Control Systems Corp. cascade impactor was used. Finally, in some experiments an in-situ measurement of the ash particle number density, velocity, and particle size distribution was desired. For these experiments, an Insitex PCSV-P was used. Each of these instruments is briefly described in the following subsections.

7.2.2.1 CCSEM

Most mineral and ash particle size and chemical composition distributions were measured by CCSEM at the University of Kentucky. For some coal and ash samples, CCSEM analysis was performed at the University of North Dakota Energy and Environmental Research Center (UNDEERC) under a co-operative agreement with DOE. CCSEM determines the size and chemical composition of at least 1200 particles per sample (2000+ at UNDEERC) by scanning the sample surface and identifying inorganic species by their high backscattered x-ray signal. Size is measured by defining a series of diagonals. Coal samples are prepared by embedding the coal in epoxy, cross-sectioning, and polishing. At the University of Kentucky, ash particles are prepared either in this manner (cross-sectioned analysis), or by dispersing the particles in triply filtered acetone with application of ultrasound, and collecting them on 0.2 μm nuclepore filters. At UNDEERC, particles are either cast and cross-sectioned as at Kentucky, or are attached to double-sided tape and mounted on an SEM stub. Samples are carbon-coated prior to analysis in all cases.

The chemical composition of individual minerals or ash particles is determined from the elemental x-ray signal emitted by each particle when excited by the electron beam. Once the elemental composition is determined, an off-line program corrects the signal for attenuation due to atomic number, absorption, and fluorescence (ZAF correction) by the application of the following correction factors- Na: 5, Mg: 2, and Al: 1.2. At UNDEERC, a full ZAF correction is performed for all elements detected. Particles are then classified by comparison with standard compositions for common minerals (e.g., quartz, pyrite) or ash particles (e.g., quartz-derived, iron oxide, etc.).

The classification schemes utilized by the two laboratories differ slightly. Whereas UNDEERC uses a single classification scheme for both coal minerals and ash particles, UKY uses differing approaches. For coal mineral analysis, UKY assigns mineral "type" - crystalline phase - identities to each mineral. For ash particles, particles are grouped according to the (up to) three major elements present. Mineral classification schemes for both groups focus on the major minerals, as shown in the abbreviated examples of each classification scheme below. A full listing of categories is provided in Appendix O.

UKY and UNDEERC: Major Coal Minerals

Pyrite
Quartz

Kaolinite
 Illite (K-Al-Silicate for UNDEERC)
 Montmorillonite
 Calcite
 Jarosite
 Gypsum
 Rutile
 Dolomite
 UKY: Miscellaneous Silicates
 UNDEERC: Ca-, Na-, and Fe-Aluminosilicates, Aluminosilicates, and Ca-Si Rich
 have been combined to provide "Misc. Silicate" category in this report.
 etc.

UNDEERC: Ash Particles, same as minerals above

UKY: Ash Particles

Fe - -
 Fe Al Si
 Si - -
 Al Si -
 K Si Al
 K Al Si
 Ca Al Si
 Al Ca Si
 Al Si Ca
 etc.

In determining the chemical composition of a given mineral, CCSEM is generally precise to within $\pm 20\%$ of a given value for minerals or compounds present in greater than 5% quantities, provided that at least 1000 particles are counted (Vleeskens and Hamburg, 1987; Zygerlicke et al., 1989). Most of the uncertainty in this measurement can be attributed to counting statistics (Huggins, 1989). For minerals present in less than 5% quantities, the error is generally of the order of the value itself (i.e., $\pm 100\%$).

Application of counting statistics to CCSEM size measurements provides a means for assessing the precision of these data as well. In this report precision for CCSEM size and composition measurements was determined in this manner, using the relation:

$$s = \frac{1}{N} \left[\frac{n_i(N-n_i)}{N} \right]^{1/2} \quad (7.1-1)$$

to obtain 2s confidence limits (approximately 95% confidence limits) for the data. s represents the standard error; N represents the total number of particles analyzed; and n_i represents the number contained in the "i"th bin.

Average chemical compositions for each major ash and mineral class as determined by CCSEM were often calculated for comparison with bulk ash compositional data. These were calculated as follows: the stoichiometric amount of oxygen was added to balance charge for each particle. Individual elements were summed for each category via

$$\text{sum} = \sum_i \frac{A f x_i \rho}{MW} \quad (7.1-2)$$

with

- A = cross-sectional area, as measured by CCSEM
- f = magnification factor (CCSEM parameter)
- x_i = atom fraction of element i
- ρ = particle density
- MW = particle molecular weight, calculated from the oxygenated composition.

and renormalized to yield the final element atom fractions. The reasoning behind this method of calculation is as follows: it has been shown that the apparent cross-sectional area fraction of each mineral, obtained from random sectioning of a uniform plug of coal/epoxy, is equal to the true volume fraction of each mineral class in the whole plug (Helble et al., 1990b). The *overall* composition of the *entire* mineral distribution can therefore be obtained from the product of the volume fraction of each mineral class (i.e., apparent cross-sectional area fraction) and the elemental composition of that class. If the composition of individual particles within a class does not vary significantly from some mean value, then the individual particles can be summed in the above fashion. Clearly this is the case for all categories save unknowns. For the unknowns, the above arguments cannot be used to justify calculation of an average composition, as the particle-to-particle composition varies widely (by definition) within this category. In simulations conducted with computer generated mineral distributions, however, it has been empirically observed that the cross-sectioned area *size* fraction of minerals in a given diameter range corresponds closely to the true volume fraction in that range, as shown for one case in Figure 7.2-5. One can therefore argue that there is justification in determining composition from the sum of individual areas, as this sum in each size fraction will correspond to the correct volume fraction. Given these arguments (and lack of a better scheme, save assigning probability density functions to each particle and computing probable overall compositions), the chemical composition of the unknown category was calculated using Eq. (7.1-2). Note that for ash particles which have not been cross-sectioned for CCSEM analysis, the area must be converted to volume by raising to the 3/2 power for this to be true (Figure 7.2-5).

FIGURE 7.2-5. - Comparison of calculated CCSEM particle size distributions, using the data in Table 7-5 of Helble et al., 1990b.

A detailed description of the CCSEM measurement technique is presented in Section 4 of this report.

The FORTRAN codes used for these calculations are presented in Appendix N.

7.2.2.2 Malvern

Measurements of the size distribution of coals, combustion-generated ash, and coal minerals (low-temperature ash samples) were also obtained with a Malvern Instruments Model 2600C laser diffraction particle sizer. Particles were dispersed in a solution of 0.15 wt% sodium pyrophosphate in distilled water, as recommended for proper dispersion of silicate-containing samples (Malvern Instruments Inc., 1985). Ultrasonic agitation of the suspension for at least 5 min duration was used to separate any loosely agglomerated particles. The sample was then diluted as needed, added to a magnetically stirred cell, and measured. Measurements were repeated until a steady state distribution was achieved, because it was noted that some samples, particularly ashes from low-rank coals, remained agglomerated during initial analysis. Two to three measurements were made per solution, utilizing two separate solutions per sample to ensure repeatability and accuracy of the measurement. The precision of these measurements was estimated to be ± 3 to 5% of the indicated values.

For certain Phase II samples, coal particle size distribution measurements were made by UNDEERC. Ethanol was used as a dispersant for these measurements.

7.2.2.3 Cascade Impactor

A Pollution Control Systems Corporation Mark III cascade impactor was used to provide on-line size segregation of the ash particles during certain experiments. Collection efficiency curves for the seven-stage impactor are shown in Figure 7.2-6. The purpose of these measurements was to measure the amount of ash present in a submicron fume. This was defined as the total mass collected on the back-up 0.2 μm filter plus that collected on stage 7 of the impactor. This definition of a submicron fume is not rigorous; it was chosen because a minimum in the differential ash mass distribution was typically noted on stage 6, suggesting different mechanisms of formation for ash collected on stage 7 and the filter. It does, however, provide a reasonable estimate of the relative amount of submicron fume generated during combustion of the program coals.

FIGURE 7.2-6. - Calculated d_{50} for PCSC Mark III Cascade impactor

7.2.2.4 PCSV-P

In selected experiments conducted at PSIT, and by PSIT at the University of Arizona (UA) and SECV, an Insittec PCSV-P was used to obtain in-situ measurements of the ash particle size distribution (number basis), ash particle velocity distribution, and ash particle number density in the flow. The instrument employs near-forward laser light scattering within the confines of a water-cooled fiber optic sampling probe to obtain these measurements in harsh environments.

Detailed information on the operating principles of this instrument are presented elsewhere (Holve, 1986). In brief, single particle scattering intensities are measured, and the overall intensity distribution subsequently deconvoluted to provide a particle size distribution (psd) without the need for assuming a shape for the psd. As shown in Figure 7.2-7, particles pass through the focus of a HeNe laser beam, scattering light into the receiver lens in proportion to their size and the local intensity of the incident beam. The scattered light is focused onto a slit aperture, and the peak height is sensed by a detector and stored. Once a statistically significant number of particles have been sampled, the peak intensities are deconvoluted to provide the final psd. Because of the Gaussian intensity profile of the beam, particle trajectories through regions of lower intensity can be accounted for.

FIGURE 7.2-7. - Schematic diagram of PCSV-P operating principle.

7.2.2.5 Neutron Activation Analysis

Selected coal and ash samples were analyzed for trace element concentrations by neutron activation analysis at MIT. Samples were collected on either polycarbonate or teflon coated polyethylene filters downstream of the cascade impactor to provide size segregated particle samples. Blank filters were also analyzed for several trace elements to determine background levels.

The application of this technique to coal and ash sample analysis has been described extensively in the open literature (e.g., Ondov et al. 1975).

7.3 Experimental Results - Phase II Baseline Study

Mineral size distributions for the Phase II coals are presented in Figures 7.3-1 and 7.3-2. The Kentucky #9 parent coal had the coarsest mineral size distribution, while two of the beneficiated coals - the Illinois #6 SOAP and the Gravimelt 9C - had the finest. Despite its 0.6% ash content, the Gravimelt 7A sample had a moderate mineral size distribution, similar to that of the Eagle Butte coal. Mineral size distributions for the Phase I coals are presented for comparison in Figures 7.3-3 and 7.3-4. The Upper Freeport bituminous coal clearly demonstrated the coarsest mineral size distribution of all coal samples considered. Note that some figures labelled "(cross-sectional) area percent" in Boni et.al. (1990) have been re-labelled "volume percent" here to avoid confusion; the two terms are equivalent for cross-sectioned samples (see discussion in Subsection 7.2).

Coal particle size distributions for the Phase II Illinois #6 parent, Illinois #6 SOAP, and Eagle Butte/Kentucky #9 blend were discussed in Section 3 of this report. Measured Malvern particle size distributions for the Loy Yang 1953, Gravimelt 7A, and Gravimelt 9C samples were not available; each was assumed to be approximately "utility grind," i.e., approximately 70% through a 200 mesh screen based upon information provided with the coal samples. Samples of Beulah and LY 1953 pulverized and tested at SECV were analyzed for coal psd's; these results are presented in Subsection 7.6 of this report. Coal particle

FIGURE 7.3-1. - CCSEM mineral size distributions for three Phase II beneficiated coals and Illinois #6 parent coal.

FIGURE 7.3-2. - CCSEM mineral size distributions for Phase II blend, blend parent coals, and Loy Yang 1953 coal.

size distributions for Phase I coals were provided in the Phase I Final Report (Boni et al., 1990) and are reproduced in Figures 7.3-5 through 7.3-7. Note that in Figure 7.3-5, Kentucky 11, Upper Freeport, and San Miguel were measured by PSIT, whereas Illinois #6 and Kentucky #9 were measured for PSIT by UNDEERC.

Ash particle size distributions obtained from combustion testing of the Phase II beneficiated coal samples are presented in Figure 7.3-8. The ash psd for a Loy Yang 1953 sample collected from the ESP during SECV tests is also shown (see Subsection 7.6). Of these coals, the Illinois #6 SOAP produced the smallest ash particles, consistent with its having the smallest mineral size distribution. Comparative ash particle size distributions obtained from combustion of Phase I coals at PSIT are presented in Figures 7.3-9 and 7.3-10. As the figure indicates, Illinois #6 bituminous produced the largest ash psd of all of the Phase I samples. This is discussed in more detail in Boni et al. (1990) and in Subsection 7.3.1 of this report.

Results for the individual coals of the Phase II study are discussed in more detail in the following subsections.

B-4070

FIGURE 7.3-3. - CCSEM mineral size distributions for Phase I low-rank coals. Error bars represent 2σ confidence interval, shown for Beulah lignite only (others are comparable).

B-4071

FIGURE 7.3-4. - CCSEM mineral size distributions for Phase I bituminous coals. Error bars represent 2σ confidence interval, shown for Kentucky #9 only (others are comparable).

FIGURE 7.3-5. - Coal particle size distribution for selected Phase I coals, measured with Malvern 2600C Particle Sizer.

FIGURE 7.3-6. - Coal particle size distribution for selected Phase I coals, measured via Malvern at EER.

B-4091

FIGURE 7.3-7. - Coal particle size distribution for Phase I coals by screen analysis.

C-2548

FIGURE 7.3-8. - CCSEM ash particle size distribution for low-ash Phase II coals.

B-4072

FIGURE 7.3-9. - CCSEM ash particle size distributions for low-rank Phase I coals. Error bars represent 2σ confidence interval for San Miguel ash; other samples are comparable.

FIGURE 7.3-10. - CCSEM ash particle size distributions for bituminous Phase I coals. Error bars represent 2σ confidence interval for Illinois #6 ash; other samples are comparable.

7.3.1 Phase II Illinois #6 and Illinois #6 SOAP

Coal, mineral, and ash analyses for the Phase II and Phase I Illinois #6 coals are presented in Table 7.3-1. Selected data from the Phase II PSIT Illinois #6 SOAP, and a sample of the Illinois #6 SOAP tested at ABB/Combustion Engineering are also presented for comparison. Examination of the first two columns of the table reveals the similarity between the two parent Illinois #6 coals. Ultimate, proximate, and ash chemical analyses for the two coals were comparable. CCSEM mineral analysis of the two Illinois #6 also demonstrated the similarity of these coals. Quartz and aluminosilicates were the dominant mineral phases in both, with significant quantities of pyrite also observed. One interesting difference was noted - while pyrite constituted 28% of the mineral matter in the Phase I coal, it represented only 14% of the Phase II coal mineral matter. The similarities in iron content and total ash content, and the presence of "miscellaneous sulfates" in the Phase II sample suggests that partial oxidation of the pyrite in the Phase II sample may have occurred. Table 7.3-2, an analysis of the major sulfur-containing mineral phases identified by CCSEM in the Phase II Illinois #6 sample, provides further evidence of sample oxidation.

Another interesting difference between the two parent coals is noted in the mineral size distributions (Figure 7.3-11). While the Phase I Illinois #6 mineral size distribution was typical of the Illinois basin coals examined (Figure 7.3-4), the Phase II sample shows a markedly finer mineral size distribution. It can be speculated that oxidation of the pyrite minerals may also be contributing to this phenomenon, producing small sulfate grains as a reaction product. Greater than 85% of the sulfate minerals observed in the Phase II parent were less than 5 μm in diameter (Table 4-7, Section 4 of this report).

Because of the similarity in coal and ash properties to the Phase I parent, combustion tests were not conducted with the Phase II Illinois #6 parent. A comparison of the chemical composition of the ash generated during combustion of the Phase I Illinois #6 with the Phase I bulk ash composition, the Phase II coal bulk ash composition, and the Phase II coal mineral composition is presented in Table 7.3-3.

A comparison of the SOAP data in Table 7.3-1 with that of the parent coals reveals changes in the fuel caused by beneficiation. In addition to the 60% reduction in ash content, a decrease in sulfur content and an increase in C/H ratio were noted. Examination of the ash chemical composition and the CCSEM-measured mineralogy indicates that quartz was removed preferentially. Note that apparent differences in mineralogy between the PSIT and ABB/CE samples are primarily the result of the samples being analyzed at different laboratories, with associated differences in mineral classification. This is generally not a problem with "raw" coals, but differences are magnified in analysis of low-ash cleaned coals such as these, where many of the minerals fall into "miscellaneous" or "partially oxidized" categories.

The ash composition determined by CCSEM was found to differ from the bulk ash composition for the PSIT SOAP sample, as shown in Table 7.3-4. Specifically, iron and aluminum oxide concentrations in the bulk ash were greater than those calculated from the

TABLE 7.3-1. - Illinois #6 SOAP and parent coal analysis

	Phase I	Phase II		
	Illinois #6	Parent Illinois #6	PSIT SOAP	ABB/CE SOAP
Proximate (wt%)				
Fixed carbon	48.6	51.5	55.5	52.8
Volatile matter	41.4	39.0	40.9	42.9
Ash	9.9	9.4	3.6	4.3
Ultimate (dry; wt%)				
C	69.1	68.3	75.3	75.7
H	5.3	4.9	5.3	5.8
N	1.6	1.2	1.4	1.5
S	4.3	3.3	2.9	2.8
O	9.8	12.9	11.4	9.9
Ash	9.9	9.4	3.6	4.3
Ash composition (wt%)				
SiO ₂	46.1	50.6	39.0	40.2
Al ₂ O ₃	18.0	21.6	18.6	19.9
TiO ₂	0.9	0.9	2.7	2.5
Fe ₂ O ₃	20.5	18.4	27.1	25.6
CaO	5.3	2.1	3.6	3.4
MgO	0.6	1.2	1.4	1.4
Na ₂ O	1.3	0.5	1.4	1.6
K ₂ O	2.1	2.1	2.4	2.4
SO ₃	4.4	2.2	3.5	2.0
P ₂ O ₅	0.1	0.0	0.2	0.2
Minerals (wt%)/Lab	UKY	UKY	UKY	UNDEERC
Quartz	20	20	11	13
Kaolinite	6	5	0	27
Illite	10	7	1	9
Misc. silicates	18	29	19	5
Misc. sulfates	-	11	14	-
Pyrite	28	14	6	28
Other	18	14	49	18

TABLE 7.3-2. - Illinois #6 coal: sulfur-containing mineral compositions (mole %)

Mineral	wt%	Al	Si	S	K	Ca	Fe
Fe sulfate	2	0	0	50	0	0	49
Miscellaneous sulfate	11	0	6	38	1	3	50
Quartz-sulfate	2	3	55	26	2	0	14
Sil.-sulfate	1	14	29	23	10	0	1
Jarosite	1	0	3	38	7	0	52

CCSEM mineral compositions. A few possible explanations can be offered for this observation. First, the generation of pyrite oxidation products may produce iron sulfate compounds that are smaller than the nominal 1 μm detection threshold of the CCSEM. These would remain undetected, yielding a low iron content in the minerals (relative to the bulk ash). Second, iron minerals may be masking some aluminosilicates in the CCSEM analysis, thus reducing the apparent aluminum concentration. In all cases, the bulk ash composition should be considered the "true" composition of the ash, whereas the CCSEM-derived data should be considered the composition of the greater than 1 μm minerals in the coal. A complete description of the mineralogy of the PSIT SOAP sample is contained elsewhere in this report (Section 4, Table 4-8).

FIGURE 7.3-11 - CCSEM mineral size distributions for Phase I and Phase II Illinois #6 bituminous coals.

TABLE 7.3-3. - Illinois #6 ash chemical composition (SO₃-free) (wt% oxides)

	Phase II Illinois #6 Bulk Ash	Phase II Illinois #6 CCSEM-Minerals	Phase I Illinois #6 Bulk Ash	Phase I Illinois #6 CCSEM-Ash
SiO ₂	52	51	49	55
Al ₂ O ₃	22	12	19	16
TiO ₂	1	0	1	1
Fe ₂ O ₃	19	31	22	12
CaO	2	3	5	11
MgO	1	0	1	0
Na ₂ O	1	0	1	0
K ₂ O	2	4	2	5

TABLE 7.3-4. - Illinois #6 SOAP ash chemical composition (wt% oxides; SO₃-free basis)

	Bulk Ash	CCSEM Minerals
SiO ₂	41	49
Al ₂ O ₃	19	12
TiO ₂	3	6
Fe ₂ O ₃	28	18
CaO	4	10
MgO	1	2
Na ₂ O	1	0
K ₂ O	3	3

The mineral size distributions for the PSIT and ABB/CE Illinois #6 SOAP samples are presented in Figure 7.3-12. The mineral size distributions for the two SOAP coals were finer than the parent Illinois #6 mineral size distributions, indicating preferential removal of the largest minerals during the cleaning process.

Because of the presence of small minerals, and the high aluminosilicate content of the ash, mineral coalescence was expected to occur during combustion. Recalling

FIGURE 7.3-12. - CCSEM mineral size distributions for PSIT Illinois #6 SOAP, ABB/CE SOAP, and Phase I and Phase II Illinois #6 bituminous coals.

Subsection 5.4.2 of this report, the low ash content may allow for some char fragmentation, so less than one ash particle per coal particle was anticipated. Combustion testing of the Illinois #6 SOAP coal was therefore conducted at 1500°C and 1250°C gas temperature in the PSIT laminar-flow drop tube furnace facility. Oxygen levels corresponding to these temperatures were 7 and 16%, determined from the model of Graham (1991) to maintain approximately constant combustion particle temperature. Figure 7.3-13 compares CCSEM-determined particle size distributions from these experiments, measured at UNDEERC on cross-sectioned samples, with the CCSEM-determined mineral distribution measured previously at the University of Kentucky. Mineral coalescence to produce larger ash particles is indicated in both cases. Note, however, that the size distributions obtained under both conditions are finer than that predicted from a 1 ash particle per coal particle model using the coal psd of Table 7.3-5, suggesting (limited) char fragmentation.

Compositional analysis of the major ash categories identified by CCSEM under both combustion conditions is presented in Table 7.3-5 for both cross-sectioned and whole particle samples. Examining the 1500°C sample first, iron aluminosilicates are the dominant composition observed, suggestive of mineral coalescence, and are enriched on the ash particle surfaces relative to the bulk. Little difference is noted between surface and interior (cross-sectional) concentration levels for the other phases identified. For the 1250°C sample, iron aluminosilicates are again dominant, and again are surface-enriched. Aluminosilicates (presumably kaolinite-derived ash particles) are depleted on the particle surface. Relative to the 1500°C results, iron aluminosilicate formation is decreased and aluminosilicate levels are

FIGURE 7.3-13. - Mineral and ash size distributions for Illinois #6 SOAP

TABLE 7.3-5. - Ash analysis of Illinois #6 SOAP by CCSEM at UNDEERC (XS area % = volume %)

	1500°C, 7% O ₂		1250°C, 16% O ₂	
	X-S	Surface	X-S	Surface
Si	3.5	5.2	3.7	7.2
Ca	0.8	0.2	3.3	0.3
K Al Si	1.4	2.1	5.1	4.4
Fe Al Si	33.3	44.1	9.1	19.0
Al Si	2.6	1.2	5.8	1.0
Si-Rich	4.5	5.2	5.6	5.1

increased at the lower gas temperature. Given the observations of iron-aluminosilicate interactions reported by the University of Arizona (Section 6 of this report), these results suggest that iron coalescence with aluminosilicates is reduced at the lower temperatures. Although oxygen levels were adjusted to maintain constant particle temperature, the difference in iron-aluminosilicate levels suggests that temperatures may have been lower at

the lower gas temperature. Particle temperature measurements would be needed to verify this. As indicated in the overall ash chemical compositions shown in Table 7.3-6, iron levels were identical in both cases as expected. Note that extraneous pyrite is not expected to be a factor in either case because it has been removed by the physical beneficiation process.

TABLE 7.3-6. Chemical composition of Illinois #6 SOAP ash by CCSEM

	1500 K Surface	1250 K Surface	1250 K Cross Section	UA-AA*
SiO ₂	49	48	43	42
Al ₂ O ₃	16	15	15	15
TiO ₂	4	4	5	-
Fe ₂ O ₃	25	24	18	35
CaO	4	5	9	3
MgO	0	0	1	1
Na ₂ O	0	0	0	1
K ₂ O	2	4	9	3
*Subsection 6.5.5.1 of this report; atomic absorption analysis				

The difference between surface and bulk iron-aluminosilicate levels can be seen more clearly in ternary CCSEM plots. An explanation of ternary diagrams is in order. In two-dimensional plots, such as Figure 7.3-14, each point on the diagram represents one or (rarely) more ash particles. The composition of each particle shown is such that the sum of the three vertices (e.g., Fe + Al + Si in Figure 7.3-14) is greater than (x) percent. (x) is typically 80, with compositions on an atom% and oxygen-free basis. Compositions are normalized prior to plotting - for example, 12% Fe, 32% Al, 36% Si would be plotted as Fe = 15, Al = 40, and Si = 45. In some ternary plots shown later in this section, a vertical bar represents the number of particles of any given composition.

Figures 7.3-14a and 7.3-14b are ternary Fe-Al-Si diagrams for the whole particle samples (surface analysis) for both conditions considered. In both cases, a wide range of iron aluminosilicate compositions is noted. In Figure 7.3-14c, a cross-sectioned sample taken from the 1250°C experiment, fewer particles and a narrower range of iron concentrations are noted. In all cases, each point represents a single ash particle with the sum Fe+Al+Si equalling at least 80 atom% of the particle on an oxygen-free basis.

As shown in Table 7.3-6, potassium levels in the cross-sectioned 1250°C sample were higher than potassium levels on the surface of the ash particles. This is reflected in the ternary diagrams of Figure 7.3-15, showing (a) the surfaces of the ash particles generated at 1500°C gas temperature; (b) the surfaces of the ash particles generated at 1250°C gas

FIGURE 7.3-14. - Fe-Al-Si ternary diagrams for Illinois 6 SOAP with $0.2 \leq dp < 80 \mu\text{m}$, $\text{Fe} + \text{Al} + \text{Si} \geq 80 \text{ atom\%}$. (a) 1500°C , 7% O_2 , ash particle surfaces; (b) 1250°C , 16% O_2 , ash particle surfaces; (c) 1250°C , 16% O_2 , cross-sectioned ash particles.

temperature; and (c) the interiors (cross-sectioned sample) of the ash particles generated at 1250°C gas temperature. Potassium concentrations are clearly greatest in Figure 7.3-15c. A possible mechanism is coating of illite-derived ash particles by iron aluminosilicates. Illite has been shown to coalesce rapidly for bituminous coals under these conditions (Boni et al., 1990), while iron appears to coalesce with the aluminosilicates more slowly. This would result in illite-derived cores coated with iron rich surfaces.

Calcium-aluminosilicate interactions are examined in the ternary diagrams of Figure 7.3-16. Low levels of calcium aluminosilicate formation are observed in surface and cross-sectioned samples at both experimental conditions. This is consistent with an Illinois #6 examined previously and is in contrast to the extensive calcium aluminosilicate formation observed for several Western coals examined previously (Boni et al., 1990).

FIGURE 7.3-15. K-Al-Si ternary diagrams for Illinois 6 SOAP ash with $0.2 \leq dp < 80 \mu\text{m}$, $K+Al+Si \geq 80 \text{ atom\%}$. (a) 1500°C , 7% O_2 , ash particle surfaces; (b) 1250°C , 16% O_2 , ash particle surfaces; (c) 1250°C , 16% O_2 , cross-sectional ash particles.

7.3.2 Loy Yang 1953

Coal, mineral, and ash analyses for the Phase II Loy Yang coal, bore # 1953 (PSIT/UA sample), and the Phase I Loy Yang coal, bore # 2301, are presented in Table 7.3-7. Each sample represents a different region of the same open cut at the Loy Yang station in Victoria, Australia. The two bore samples were similar to one another on a dry basis, as is apparent from examination of the upper portion of the table. One significant difference can be found in the ash content of the two coals. On a dry basis, Loy Yang 1953 contains 2.9% ash, while Loy Yang 2301 contains only 1.4% ash. Differences also can be found in the ash chemical composition. Although most constituents are present in comparable amounts, sodium and chlorine represent a smaller percentage of the ash in Loy Yang 1953. The sodium to silicate ratio in Loy Yang 1953 is therefore considerably smaller

FIGURE 7.3-16. - Ca-Al-Si ternary diagrams for Illinois 6 SOAP ash with $0.2 \leq dp < 80 \mu m$, $Ca+Al+Si \geq 80$ atom%. (a) $1500^{\circ}C$, 7% O_2 , ash particle surfaces; (b) $1250^{\circ}C$, 16% O_2 , ash particle surfaces; (c) $1250^{\circ}C$, 16% O_2 , cross-sectioned ash particles.

than in Loy Yang 2301, suggesting that a smaller fraction of sodium would reside in the submicron fume for LY 1953 (see discussion in Section 6 of this report).

CCSEM mineral analysis of the two coals also demonstrated more similarities than differences. Although quantitative analysis of the Loy Yang 2301 was not obtained because of difficulty analyzing low ash coals during Phase I, the major minerals observed in LY 2301 - quartz, silicates, and oxidized iron species - were also present in LY 1953. This is shown in the bottom portion of Table 7.3-6.

Substantial differences were noted, however, when the LY 1953 samples examined at PSIT/UA and SECV were compared. Although quartz and mixed aluminosilicate phases

TABLE 7.3-7. - Coal, mineral, and ash analysis for Loy Yang coals

	Loy Yang (1953)*	Loy Yang (2301)**
Proximate (wt%)		
Fixed carbon	30.4	41.6
Volatile matter	36.1	44.2
Ash	2.0	1.3
Moisture	31.5	12.9
Ultimate (dry, wt%)		
C	64.2	67.3
H	4.6	4.8
N	0.9	0.5
S	0.4	0.3
O (difference)	27.0	25.7
Ash	2.9	1.4
Ash composition (wt%)		
SiO ₂	11.8	9.4
Al ₂ O ₃	5.2	4.7
TiO ₂	0.3	0.7
Fe ₂ O ₃	15.9	16.3
CaO	3.4	3.8
MgO	22.2	14.5
Na ₂ O	13.5	30.7
K ₂ O	0.7	0.7
SO ₃	26.5	19.3
P ₂ O ₅	0.5	—
Chlorine[†] (ppm)	3200	5000
Minerals (wt%)/Lab	UKY	UKY
Quartz	43	✓
Misc. silicates	24	✓
Illite	-	Minor
Fe-rich	11	✓
<p>*Ult/prox/ash analysis by UNDEERC. PSIT coal sample. **Analysis by SECV, numbers CS/87/256 and CS/88/59. †Analysis by Galbraith Analytical Labs on as-received samples.</p>		

were present in both samples, the amount of oxidized iron phase was much greater in the sample tested in the SECV pilot scale facility (Table 7.3-8). During the testing, the presence of large pieces of iron oxide at the bottom of the sample barrel were noted. It was assumed that these contaminated the test #1 sample, so this test was repeated as test #4. It is the test #4 coal that was examined by CCSEM; the resulting analysis suggests that this coal may also have been contaminated by some large pieces of iron oxide. For this reason, the PSIT/UA

TABLE 7.3-8. - Loy Yang 1953 CCSEM mineral analysis

	PSIT Sample	SECV* Sample
Quartz	43	23
Misc. silicate	24	8
Mix. carb.	2	4
Pyrite	0	6
Fe-rich	11	43
*Iron-contaminated; see Subsection 7.6 discussion. Complete analysis in Table 4-5.		

sample was taken to be the baseline coal for the tests conducted at SECV as well. A further comparison of the PSIT/UA and SECV samples is presented in Table 7.3-9. More discussion is also provided in the pilot test section (7.6) of this report.

Combustion tests were conducted with Loy Yang 1953 brown coal at PSIT, the University of Arizona, MIT, and the SECV. The MIT tests utilized size-fractionated coal samples, focusing on the importance of char fragmentation and submicron fume formation during combustion. These results were discussed in Subsection 5.4.1. The PSIT, UA, and SECV tests, however, all utilized "utility grind" (nominal 70 to 80% through a 200 mesh screen) coal samples. CCSEM ash particle size distributions obtained from the UA and PSIT/SECV tests are compared with the coal mineral size distribution in Figure 7.3-17. The ash particle size distributions at both UA and SECV were comparable, demonstrating a very slight increase relative to the mineral psd. These distributions are suggestive of limited coalescence - i.e., each mineral forming an individual ash particle. The presence of a significant amount of organically associated species, which can contribute to the formation of small ash particles, makes interpretation of the exact extent of coalescence difficult.

The chemical composition of the ash can also be used as a fingerprint for coalescence. Although significant sulfation was observed in the UA ash sample, there was little evidence of aluminosilicate formation (Subsection 4.5.4). Nor was there evidence for aluminosilicate formation in the PSIT/SECV samples (Subsection 7.6), again suggesting that mineral coalescence was limited for this coal. While *mineral* coalescence may not have occurred for this coal, the interaction of minerals with organically associated inorganic species was found

TABLE 7.3-9. - LY 1953 CCSEM mineral size distributions

Mineral Species	UA/PSIT Sample							
	wt%	0.0 2.5	2.5 5.0	5.0 10.0	10.0 20.0	20.0 40.0	40.0 80.0	80.0 500.0
Quartz	43.3	12.0	59.0	6.0	17.0	3.0	3.0	0.0
Misc. silicates	23.6	13.0	81.0	1.0	3.0	0.0	1.0	0.0
Fe-rich	10.8	4.0	3.0	2.0	7.0	6.0	37.0	41.0
Misc. mixed	14.3	18.0	78.0	1.0	2.0	1.0	0.0	0.0
Minor minerals	8.0	57.0	30.0	1.0	2.0	2.0	2.0	7.0
Grand totals	100.0	16.0	59.0	3.0	9.0	2.0	6.0	5.0
SECV Sample (contaminated)								
Quartz	23.1	11.0	20.0	6.0	10.0	6.0	15.0	32.0
Misc. silicates	7.8	15.0	31.0	14.0	4.0	5.0	14.0	17.0
Fe-rich	42.5	3.0	9.0	3.0	9.0	4.0	8.0	63.0
Misc. mixed	12.4	21.0	59.0	8.0	10.0	2.0	0.0	0.0
Minor minerals	14.2	51.0	27.0	10.0	10.0	3.0	0.0	0.0
Grand totals	100.0	15.0	22.0	6.0	9.0	4.0	8.0	35.0

to occur. In Table 7.3-10, the chemical composition of the bulk ash, minerals (PSIT/UA sample), modified minerals (subtracting all iron-rich minerals > 80 μ m), PSIT/SECV ESP ash sample, UA ash sample, and UA total ash sample (collected from a total filter and analyzed by AA spectroscopy) are compared. First, differences between the bulk ash and the minerals - columns one and two - reveal the presence of a significant quantity of organically associated sodium and magnesium for this coal. Comparing the mineral analysis with the PSIT/SECV test results, extensive interaction of the organically associated species is evident. This is also apparent in the UA impactor stage 1 sample; interestingly, calcium (sulfate) was also observed. The source of this calcium is unclear. Although contamination was suspected, the prior experiment at UA utilized Loy Yang 2301, also low in calcium.

To determine the amount of submicron fume formed during combustion of Loy Yang 1953, ash was also collected with a cascade impactor during combustion experiments at PSIT and UA. Size distributions obtained at PSIT utilized a Pollution Control Systems Mark III

FIGURE 7.3-17. - CCSEM mineral and ash particle size distributions for PSIT/UA Loy Yang 1953, SECV Loy Yang 1953, UA combustion ash (impactor stage 1), and PSIT/SECV combustion ash (ESP hopper sample, test number 4).

TABLE 7.3-10. - Loy Yang 1953 ash chemical composition (wt% oxides; SO_3 -free basis)

	Bulk Ash	CCSEM Minerals	Modified* Mineral	PSIT-SECV** CCSEM Ash	UA† IM1 CCSEM	UA-AA†† Ash
SiO_2	16	49	64	5	14	39
Al_2O_3	7	3	3	27	18	2
TiO_2	0	1	1	1	3	-
Fe_2O_3	22	44	27	7	11	35
CaO	5	2	2	6	39	3
MgO	31	0	0	24	3	5
Na_2O	18	0	0	28	10	16
K_2O	1	0	0	1	3	0
*CCSEM; minerals $\geq 80 \mu\text{m}$ excluded **ESP hopper sample, test 4 †Subsection 6.5.4.4 of this report ††Stage 1 of impactor						

Cascade Impactor subsequent to combustion of LY 1953 in 7% oxygen at 1675 K (approximate) bulk gas temperature (wall temperature = 1773 K). Results are shown in Figure 7.3-18. Under these conditions, most of the ash mass was present in $> 8 \mu\text{m}$ residual ash particles; approximately 10% of the ash formed a submicron fume. At higher particle combustion temperatures generated by an increase in oxygen level to 21% O_2 in N_2 , a slight increase, to approximately 15% in the submicron fraction, was observed (Figure 7.3-19). This is significantly less than the 40+ % of ash mass in the fume observed

FIGURE 7.3-18. - Cascade impactor results, Loy Yang 1953, 7% oxygen

FIGURE 7.3-19. - Cascade impactor results, Loy Yang 1953, 21% oxygen, 1700 K

previously for LY 2301 at 1500 K, 21% oxygen at PSIT, shown in Figure 7.3-20. In tests conducted at UA utilizing an Andersen Mark III Cascade Impactor, and combustion conditions of 1400 K peak flame temperature, stoichiometric ratio = 1.2, similar results were obtained (Table 7.3-11). The reduction in submicron ash mass relative to Loy Yang 2301 is attributed to the greater mineral (and silicate) content of the LY 1953.

FIGURE 7.3-20. - Cascade impactor PSD, Loy Yang 2301, 21% O₂, 1500 K

TABLE 7.3-11. - Loy Yang 1953 ash particle size distributions

Stage No.	PSIT*		UA**	
	dp	wt%	dp	wt%
1	> 8 μm	73-75	> 9.0	79
2		-	5.8	2
3	4.8	5-7	4.7	1
4	2.2	5-7	3.3	1
5	1.2	5-6	2.1	1
6	0.7	2-4	1.1	2
7	0.4	0	0.65	2
8	0.2	0-1	0.43	5
FF	-	8-10		8

*1700 K, 7% O₂
**1400 K, SR = 1.2

Loy Yang 1953 is discussed further in:

Subsection 7.6	PSIT/SECV Testing;
Subsection 6.5.4.4	UA Test Burn 50;
Subsection 5.4.1.2	MIT Baseline Test Results;
Subsection 4.5.4	CCSEM Results; and
Subsection 3.3.3	Loy Yang Coal Analysis.

Test results for the Loy Yang 2301 sample were discussed at length in Subsections 8.3.3.8, 7.4.7, and 6.5.2.2 of the Phase I Final Report (Boni et al., 1990).

7.3.3 Eagle Butte/Kentucky #9 Blend

Coal, ash, and mineral analyses for the Phase I and Phase II Eagle Butte coals, and the Phase I and Phase II Kentucky #9 coals are presented in Table 7.3-12. For both coal types, the ultimate and proximate analyses of the Phase I and Phase II samples were in good agreement. The chemical composition of the ash was also comparable for the Phase I and II samples of each coal as shown in the center portion of the table. Some differences in coal mineralogy between Phase I and Phase II samples were indicated by CCSEM. For both the Eagle Butte and the Kentucky #9, pyrite levels were higher in Phase II samples than in Phase I samples. Because pyrite levels in Phase I samples were low for the amount of iron reported in the ash, Phase II values are considered more reliable. It is speculated that the difference in pyrite levels may also, at least in part, be a result of the slightly different mineral classification schemes used at the University of Kentucky (Phase I samples) and UNDEERC (Phase II parent and blend samples). This latter point cannot be confirmed without further analysis.

CCSEM mineral size distributions for the Phase II and Phase I parent coals are presented in Figure 7.3-21. As is clearly indicated, the mineral size distribution for the Phase II Eagle Butte was considerably finer than for the Phase I Eagle Butte. Mineral size distributions for the Phase I and Phase II Kentucky #9 coals were comparable, with the Phase II sample having a slightly coarser mineral size distribution.

As discussed in Subsection 3.3.4 of this report, a 70/30 wt% Eagle Butte/Kentucky #9 blend was prepared from these two parent coals. Ultimate and proximate analyses confirmed that a blending ratio of 70/30 was achieved. Coal and ash analyses presented in Table 7.3-13 demonstrate that the blend was a moderate ash (7.3%) coal, with ash chemistry dominated by silica, iron (pyrite), and calcium (organically associated, from the Eagle Butte). Mineralogical analysis, presented at the bottom of the table, confirmed the presence of quartz, aluminosilicates, and pyrite. From the mineral distribution in Figure 7.3-22, the small size of the minerals - comparable to the mineral size distribution for the parent Eagle Butte - is apparent. Note that the pyrite level in Table 7.3-13 is too high given the iron content of the coal, and too high given the pyrite content of the parent Eagle Butte and Kentucky #9 coals. This suggests that a few large pyrite particles may have biased the CCSEM analysis of the blend toward higher pyrite concentrations; additional analysis would be necessary to confirm this.

TABLE 7.3-12. - Eagle Butte and Kentucky #9 parent coal analysis (dry basis)

	Eagle Butte		Kentucky #9	
	Phase I	Phase II	Phase I	Phase II
Proximate (dry, wt%)				
Fixed carbon	48.4	46.1	46.8	45.2
Volatile matter	45.1	48.1	37.6	39.9
Ash	6.4	5.8	15.6	14.8
Ultimate (dry, wt%)				
C	67.2	71.2	65.4	68.2
H	5.0	5.1	4.7	4.8
N	1.4	0.9	1.8	1.3
S	0.5	0.5	3.9	4.4
O (difference)	19.5	16.6	8.6	6.5
Ash	6.4	5.8	15.6	14.8
Ash composition (wt%)				
SiO ₂	28.4	23.8	44.6	41.5
Al ₂ O ₃	15.5	14.0	20.6	18.1
TiO ₂	0.9	1.3	1.1	0.6
Fe ₂ O ₃	6.1	5.9	22.4	22.3
CaO	26.4	25.7	3.1	7.0
MgO	6.2	9.0	1.1	1.4
Na ₂ O	2.0	1.2	0.9	0.7
K ₂ O	0.2	0.3	2.6	1.8
SO ₃	13.7	18.1	4.7	6.1
P ₂ O ₅	0.7	0.8	0.1	0.5
Minerals (wt%)/Lab	UKY	UNDEERC	UKY	UNDEERC
Quartz	40	31	12	9
Kaolinite + misc. silicate	29	35	40	14
Illite	2	1	23	19
Pyrite	4	11	16	37

FIGURE 7.3-21. - CCSEM mineral size distributions for Phase II Eagle Butte, Phase I Eagle Butte, Phase II Kentucky #9, and Phase I Kentucky #9 coals.

Combustion experiments with the Phase II Eagle Butte, Phase II Kentucky #9, and 70/30 blended coals were performed in the PSIT externally heated drop tube reactor facility. Coal samples were nominally utility grind, as discussed in Subsection 3.3.4. For these experiments, the drop tube furnace was operated at a wall temperature and oxygen composition of 1750 K and 7% O₂ in N₂, respectively. CCSEM analysis of the combustion-derived ash was analyzed by UNDEERC, on both a cross-sectioned and a particle surface basis. Cross-sectioned samples were embedded in epoxy and sectioned as the term implies. Cross-sectioned results could be compared directly with mineral size distributions because both are on the same cross-sectioned basis. Particle surface samples were analyzed by dispersing the ash particles on a filter and analyzing them without sectioning. This provided information on the composition of the outer few micrometers of a particle; distributions, however, must be inverted to derive continuous particle size distributions for comparison with mineral size distributions. Ash particle size distributions were also determined by Malvern analysis.

Cumulative volume distributions of ash generated from combustion of the blend (70% EB/30% Ky9) and its two parent coals are shown in Figure 7.3-23. The distributions were obtained with a Malvern particle sizer, using a lens of focal length 63 mm. The distributions were not additive as expected; in fact, the ash particle size distribution for the blend was smaller than the ash particle size distributions of either of the parent coals. The observed ash distribution from the Eagle Butte coal was comparable to that expected, assuming complete coalescence (1 ash particle generated per coal particle) and an Eagle Butte

TABLE 7.3-13. - Eagle Butte/Kentucky #9 coal blend analysis

	Blend (Measured)
Proximate (wt%)	
Fixed carbon	36.3
Volatile matter	34.5
Ash	7.3
Moisture	21.8
Ultimate (dry, wt%)	
C	68.8
H	5.0
N	1.0
S	1.9
O (difference)	13.9
Ash	9.4
Ash composition (wt%)	
SiO ₂	30.1
Al ₂ O ₃	15.1
TiO ₂	0.9
Fe ₂ O ₃	14.2
CaO	15.8
MgO	3.3
Na ₂ O	1.2
K ₂ O	1.2
SO ₃	17.7
P ₂ O ₅	0.6
Minerals (wt%)/Lab	UNDEERC
Quartz	11
Kaolinite + misc. silicate	15
Illite	15
Pyrite	39

FIGURE 7.3-22. - CCSEM mineral size distributions for Phase II Eagle Butte, Phase II Kentucky #9, and Phase II 70/30 Eagle Butte/Kentucky #9 blend. Mineral size distributions by UNDEERC; Zygarlicke et al. (1992).

FIGURE 7.3-23. - Cumulative ash volume distributions obtained by Malvern analysis.

coal particle size distribution equivalent to the blend coal particle size distribution given in Table 7.3.13 (see Figure 7.3-24). Thus, while the actual Eagle Butte ash psd may be smaller due to char fragmentation or incomplete coalescence, and while inadequate sample dispersion in the Malvern measuring fluid (sample agglomeration) may have masked this, it cannot be concluded from the measurements. The measured ash psd would need to have been greater than the 1 ash per coal psd for confirmation.

The size distributions of ash obtained by CCSEM analysis, however, showed different trends. Figure 7.3-25 shows the cumulative volume distributions of ashes from the combustion of Kentucky No. 9, Eagle Butte and blend coals. Cross-sectioned ash samples were used to make this plot. While the Eagle Butte and Kentucky #9 ash particle size distributions were again shown to be comparable, the blend ash particle size distribution was larger than the ash psd of either parent coal. This is in contrast to the Malvern analysis of these ashes, which showed the blend ash to be smaller than either of the two parent coal ashes. If the CCSEM analysis is to be believed, the results suggest possible agglomeration of the two parent coals during the laboratory combustion experiments. While possible, however, this is considered unlikely. Agglomeration would be driven by collision with plasticizing Kentucky #9 coal particles; if occurring for the blend, it should have been occurring for the Kentucky #9 parent as well.

FIGURE 7.3-24. - Comparison of measured Eagle Butte ash particle size distribution (Malvern analysis) and a distribution calculated assuming that one ash particle is generated per coal particle.

FIGURE 7.3-25. - CCSEM particle size distributions for ash generated from combustion of Phase II Eagle Butte, Phase II Kentucky #9, and 70/30 Eagle Butte/Kentucky #9 blend. Cross-sectional analysis.

The ash distribution comparison, while demonstrating the similarity of the Kentucky #9 and Eagle Butte ash size distributions, was inconclusive for the blend in that the two size analysis methods showed different trends. CCSEM analysis of the ash chemical composition, as well as more detailed examination of the individual coal mineral and ash size distributions, can be used to address this apparent discrepancy in more detail. This is discussed in the following subsections.

7.3.3.1 Eagle Butte Results

Mineral and ash size distributions for the Phase II Eagle Butte coal, determined by CCSEM analysis at UNDEERC, are presented in Figure 7.3-26. Ash particle size distributions measured on both a cross-sectioned ash sample and on a dispersed ash sample, corrected to be on a consistent basis, were comparable. When compared with the mineral size distribution, coalescence of the smallest mineral inclusions was indicated.

The chemical composition distribution of the ash can also be used to evaluate the extent of coalescence occurring among inorganic species during combustion. Table 7.3-14 identifies the major compositional categories identified in the Eagle Butte coal minerals, on the surface of the ash particles, and in the core of the ash particles (cross-section). Quartz and kaolinite were the dominant mineral phases in this coal, representing over 60% of the mineral matter. After combustion in the PSIT laboratory furnace, the ash revealed much

FIGURE 7.3-26. - CCSEM particle size distributions for Phase II Eagle Butte minerals and combustion generated ash produced in 7% oxygen at 1700 K. Ash cross-sectional analysis and corrected surface analysis are both shown.

TABLE 7.3-14. - CCSEM analysis of Eagle Butte Phase II ash (by UNDEERC)

Mineral Phase/ Ash Composition	Mineral	X-S Ash	Ash
Quartz/Si	31	5	7
Kaolinite/Al Si	31	5	3
Illite/K Al Si	1	0	0
Calcite/Ca	0	0	1
Ca Al Si	1	14	13
Ca Al	0	13	11
Pyrite/-	11	0	0
Fe Al Si	0	0	0
Fe oxide	2	0	0
Na Al Si	-	4	8

lower concentrations of silica-rich and aluminosilicate-rich regions. Instead, calcium rich phases became dominant. Sodium aluminosilicates have also appeared. In both cases, formation of these phases is indicative of the coalescence of aluminosilicate minerals with organically associated calcium and sodium.

From the CCSEM-measured composition of individual ash particles, it is possible to determine the overall composition of the ash, both on the surface and in the particle cores (cross-sectioned analysis). This analysis for the Phase II Eagle Butte ash is compared to the coal bulk ash composition (Table 7.3-12) in Table 7.3-15. Examining the first three columns of the table, silicon appears to be slightly enriched and calcium slightly depleted in the particle centers. Looking further at size-segregated ash samples, calcium concentrations were high in both the core and on the surface of all ash particles $< 5 \mu\text{m}$ in diameter. Silicon concentrations were correspondingly low, while aluminum concentrations were comparable to those in the bulk ash. These results are indicative of calcium aluminosilicate formation in the smallest ash particles. The increased calcium concentration provides a marker for calcium coalescence, while the constant aluminum and decreased silicon suggest that aluminosilicates rather than silica were coalescing with the calcium. The corresponding decrease in calcium and increase in silicon in the largest ash particles suggests that quartz particles $> 5 \mu\text{m}$ were not reacting extensively with the organically associated species. Thus, it can be concluded that for the Phase II Eagle Butte, small aluminosilicate minerals and small quartz coalesced extensively with organically bound calcium. Coalescence of the larger minerals was more limited, as evidenced by the high silicon content of the largest ash particles. Similar evidence of calcium aluminosilicate formation was noted in testing of the Phase II Eagle Butte as shown in Figure 7.3-27 (Boni et al., 1990). As discussed previously, this figure is a ternary representation of all ash particles containing at least 80 mole% of the indicated elements - in this case, Ca + Al + Si - on an oxygen-free basis.

TABLE 7.3-15. - Eagle Butte ash chemical composition (wt% oxides)

	Coal Bulk Ash	CCSEM Combustion Ash	X-S CCSEM Combustion Ash	CCSEM Combustion Ash ($0.1 < dp \leq 5 \mu\text{m}$)	X-S CCSEM Combustion Ash ($0.1 < dp \leq 5 \mu\text{m}$)	CCSEM Combustion Ash ($dp > 5 \mu$)
SiO ₂	29	31	24	24	22	44
Al ₂ O ₃	17	18	19	21	21	12
TiO ₂	2	3	3	2	3	6
Fe ₂ O ₃	7	4	4	4	3	5
CaO	32	37	44	42	44	27
MgO	11	4	4	5	5	4
Na ₂ O	1	1	1	1	1	1
K ₂ O	1	1	1	1	1	1

(a) 1650 K gas temperature

(b) 1500 K gas temperature

FIGURE 7.3-27. - Ca-Al-Si ternary diagram for ash generated during combustion of Phase I Eagle Butte coal in 7% oxygen.

Each point represents at least one ash particle of a given composition. In other ternary diagrams where a vertical dimension is also indicated, the height of each peak represents the number of particles of a particular composition.

7.3.3.2 Kentucky #9 Results

Mineral and ash size distributions for the Phase II Kentucky #9 coal, determined by CCSEM analysis at UNDEERC, are presented in Figure 7.3-28. Ash particle size distributions measured on both a cross-sectioned ash sample and on a dispersed ash sample, corrected to be on a consistent basis, were comparable and were smaller the measured mineral size distribution. This result, suggestive of mineral fragmentation, differs from that obtained with the Phase I Kentucky #9, where coalescence was indicated. It is, however, consistent with the presence of large pyrite minerals that are prone to fragment, previously speculated to exist in the blend and in this coal.

As with the Eagle Butte, the chemical composition distribution of the ash can be used as an indicator for coalescence during combustion. Table 7.3-16 identifies the major compositional categories identified in the Kentucky #9 coal minerals, on the surface of the ash particles, and in the core of the ash particles (cross-section). As discussed previously, pyrite was the major mineral phase present, with significant amounts of illite and kaolinite

FIGURE 7.3-28. - CCSEM particle size distributions for Phase II Kentucky #9 minerals and combustion generated ash produced in 7% oxygen at 1700 K. Ash cross-sectional analysis and corrected surface analysis are both shown.

TABLE 7.3-16. - CCSEM analysis of Kentucky #9 Phase II ash (by UNDEERC)

Mineral Phase/ Ash Composition	Mineral	X-S Ash	Ash
Quartz/Si	9	15	14
Kaolinite/Al Si	11	13	19
Illite/K Al Si	19	17	15
Calcite/Ca	8	1	2
Ca Al Si	0	4	2
Ca Al	0	0	0
Pyrite/-	37	0	0
Fe Al Si	1	8	9
Fe oxide	0	5	2

also observed. In the combustion-derived ash, limited formation of iron aluminosilicates was observed. A similar phenomenon was observed during combustion of the Phase I Kentucky #9 coal (Figure 7.3-29). Otherwise, little interaction among the minerals was noted. Quartz, kaolinite, and illite levels all remained constant. No differences were noted between the surface and the core of the ash particle either, again suggesting little interaction among the minerals. A high concentration of excluded minerals or extensive char fragmentation could both contribute to the observed lack of interaction. A similar conclusion can be drawn from analyzing the CCSEM-determined ash chemical compositions shown in Table 7.3-17.

7.3.3.3 Blend Results

CCSEM mineral and ash size distributions for the 70/30 Eagle Butte/Kentucky 9 blend coal are presented in Figure 7.3-30. For this coal, the ash particle size distribution measured on the cross-sectioned ash sample was in good agreement with that measured for the dispersed ash sample for particles greater than 20 μm only. At smaller sizes, a much finer ash particle size distribution was measured for the cross-sectioned sample. Note that this distribution was comparable to one calculated under the assumption that one ash particle was generated per coal particle, with uniform distribution of ash among all coal particle sizes. The coal particle size distribution in Table 3.13 was used as the basis for this calculation. Both CCSEM size distributions were greater than the mineral distribution measured for this coal.

Recalling the discussion in the previous two subsections, mineral coalescence was noted for the Eagle Butte coal, while mineral coalescence was not noted for the Kentucky #9. Because the Eagle Butte represents 70% of the blend, significant coalescence was expected.

FIGURE 7.3-29. - Fe-Al-Si ternary diagram for ash generated during combustion of Phase I Kentucky #9 coal in 7% oxygen.

TABLE 7.3-17. - Kentucky #9 ash chemical composition (SO₃-free) (wt% oxides)

	Coal Bulk Ash	CCSEM Combustion Ash	X-S CCSEM Combustion Ash	CCSEM Combustion Ash (0.1 < dp ≤ 5 μm)
SiO ₂	44	60	58	57
Al ₂ O ₃	19	19	20	22
TiO ₂	1	2	2	2
Fe ₂ O ₃	24	10	12	10
CaO	8	5	4	5
MgO	1	0	0	0
Na ₂ O	1	1	1	1
K ₂ O	2	3	3	3

FIGURE 7.3-30. - CCSEM particle size distributions for blend minerals and combustion generated ash produced in 7% oxygen at 1700 K.

As the size distributions in Figure 7.3-30 and the ash chemical analysis in Tables 7.3-18 and 7.3-19 show, coalescence was indeed noted. Calcium aluminosilicate formation was noted at levels comparable to those observed in the parent Eagle Butte. Decreases in kaolinite and quartz concentrations were also noted. Interestingly, a decrease in illite concentration, while not observed for the parent Kentucky #9, was observed for the blend. Ash chemical composition data, calculated from CCSEM analysis of the ashes, revealed silica enrichment in particle cores and iron enrichment on particle surfaces, particularly those greater than 5 μm in diameter. This may be indicative of the agglomeration of large iron oxide particles with aluminosilicate ash particles, as was discussed previously in Subsection 6.8 of this report. Some formation of alkali and alkaline earth aluminosilicates was also observed, although there was no increase in concentration noted on the particle surfaces relative to the cores. This is seen in the ternary diagrams of Figure 7.3-31. Comparing the surface and cross-sectioned samples, little difference is noted in the (Ca+Na+K+Mg) region of the diagram.

The blending of coals is used as a way to reduce sulfur emissions while using high sulfur content coals. This is achieved by reducing the total emission of sulfur per energy generated by diluting the high sulfur content coal with low sulfur content coal(s). In addition to this, sulfur may be captured by the ash formed during coal combustion if appropriate coals (e.g., coals with high alkali and alkaline earth metals) are used for the dilution.

TABLE 7.3-18. - CCSEM analysis of blend combustion-generated ash

Mineral Phase/ Ash Composition	Mineral	X-S Ash	Ash
Quartz/Si	11	9	9
Kaolinite/Al Si	13	11	4
Illite/K Al Si	15	5	3
Calcite/Ca	8	3	8
Ca Al Si	0	14	11
Ca Al	0	2	3
Pyrite/-	39	0	0
Fe Al Si	1	1	2
Fe Oxide	0	2	7
Na Al Si	-	2	2

TABLE 7.3-19. - Blend ash chemical composition (SO₃-free) (wt% oxides)

	Coal Bulk Ash	CCSEM Combustion Ash	X-S CCSEM Combustion Ash	CCSEM Combustion Ash (dp ≤ 5 μm)	X-S CCSEM Combustion Ash (dp ≤ 5 μm)	CCSEM Combustion Ash (dp > 5 μm)
SiO ₂	37	32	43	30	41	33
Al ₂ O ₃	19	10	19	17	20	9
TiO ₂	1	2	2	2	2	2
Fe ₂ O ₃	17	33	9	20	9	35
CaO	20	20	21	26	23	18
MgO	4	1	2	2	2	1
Na ₂ O	1	0	1	1	1	0
K ₂ O	1	1	2	1	2	2

(a) Blend (cross-sectioned, all sizes)

(b) Blend (cross-sectioned, dp > 10 μ m)

(c) Blend (whole, all sizes)

(d) Blend (whole, dp > 10 μ m)

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FIGURE 7.3-31. - (Alkali+alkaline earth) - Al - Si ternary diagrams for blend coal ash.
Each point represents at least one ash particle, with the sum $X+Al+Si > 80$ mole%
of the composition on an oxygen-free basis.

ASTM ash analysis data show that the Eagle Butte sub-bituminous coal ash contained a significant amount of CaO (26% of the ash). The calcium-rich ash from the Eagle Butte coal can play an important role for further reduction of sulfur emissions from the pyrite-rich Kentucky No. 9 coal. A simple calculation was carried out to determine the amount of sulfur captured by the greater-than-1 μm , calcium-rich ash particles examined by CCSEM. Table 7.3-20 shows the total ash composition by oxide weight percentages for the ash from the three coals calculated by examining the CCSEM surface analysis data. Note that the data in this table differs slightly from that presented in Quarterly Report #20, as an error was recently discovered in the labeling of the CCSEM analysis for these surface samples. Comparison of the three columns in the table shows that a small amount of sulfur was captured by the ash for the blended coal, which suggests that the calcium-rich ash provided by the Eagle Butte coal was acting as a sulfur sorbent.

TABLE 7.3-20. - Ash compositions of Eagle Butte, Kentucky No. 9, and blend coals by oxide weight percentages

Oxides	Eagle Butte	Kentucky No. 9	Blend
Na ₂ O	0.7	0.4	0.3
MgO	4.4	0.2	1.2
Al ₂ O ₃	17.6	19.0	9.4
SiO ₂	30.6	59.1	30.4
P ₂ O ₅	0.5	0.3	0.4
SO ₃	1.1	0.9	4.8
K ₂ O	0.5	2.6	1.4
CaO	35.7	5.0	18.4
Fe ₂ O ₃	4.2	9.8	30.7
TiO ₂	3.4	1.6	2.42

In order to investigate the interaction of the ash particles with the sulfur, further analysis on the CCSEM data was carried out. Figure 7.3-32 (a), (b), and (c) show the ternary diagrams of sulfur-containing ash particles for Kentucky No. 9, Eagle Butte, and the blend coals, respectively. The components examined in the ternary diagrams are sulfur (S), silicon and aluminum (Si-Al), and major alkali and alkaline earth metals (Ca, K, Na, and Mg). Figure 7.3-32 (a) shows that sulfur-containing ash from Kentucky No. 9 coal is mainly aluminosilicate particles. Figure 7.3-32 (b) on the other hand, shows that sulfur-containing ash particles from Eagle Butte coal have a wider variation in composition. Figure 7.3-32 (c) shows a combination of the two parent coals. Interaction of sulfur with ash particles can take place by two mechanisms (Graham, 1991): sulfation of ash and heterogeneous condensation of sulfur onto existing ash surfaces. Alkali- and alkaline-earth-rich ash particles can and probably do incorporate sulfur by the sulfation of the ash. Aluminosilicate particles probably incorporate sulfur by heterogeneous condensation of SO₂. This being the case, Kentucky No.9 ash particles may acquire sulfur by condensation whereas Eagle Butte ash particles acquire sulfur both by sulfation and condensation. Blending of these two coals shows both of the trends. Also noticed in the blend ash diagram is that as the alkali and alkaline earth metal composition increases so does the sulfur content.

FIGURE 7.3-32. - Ternary diagram ((Ca + Na + K + Mg) - (Si + Al) - S) of all ash particles containing sulfur produced by the combustion of the blended coal at 1700 K, 7% O₂.

Figure 7.3-33 shows the interaction of calcium with sulfur in a different plot in terms of calcium (Ca), aluminum (Al), and silicon (Si) for sulfur containing ash particles. Figure 7.3-33 leads to the same conclusions on the mechanisms. Figure 7.3-34 shows the effect of the calcium content on the amount of sulfur captured. Figures 7.3-34 (a), (b), and (c) show the compositions of whole ash particles from the blend coals at various levels of sulfur content: greater than 0 mole% (all sulfur containing particles), greater than 5 mole%, and greater than 10 mole%, respectively. It is shown that as the amount of calcium in ash increases, so does the amount of sulfur captured. This trend identifies the sulfation of calcium-rich ash particles.

In conclusion, from analysis of the parent and blended coals combustion test data, it can be concluded that:

- organically bound calcium and sodium coalesced with aluminosilicate minerals during combustion of the Eagle Butte;
- no coalescence was observed for the Kentucky #9 coal minerals;
- the behavior of the blend generally followed that of the major component in the blend (Eagle Butte), with coalescence indicated by size and composition distributions;
- ash particle compositional analysis did not provide any evidence of interaction between the coals or their ashes during combustion or sampling; size distribution data was, however, inconclusive on this point, with Malvern and CCSEM providing contradictory results.
- sulfur concentrations in the ash were greatest for samples collected during combustion testing of the blend, suggesting that calcium and other species from the sub-bituminous coal were able to capture sulfur produced during combustion of the bituminous coal.

Combustion testing and analysis of the 70/30 wt/wt blend of Eagle Butte sub-bituminous and Kentucky #9 bituminous coals is discussed further in:

Subsection 6.5.5.3 UA Test Burns 59 and 60;
Subsection 5.4.1.2 MIT Baseline Test Results;
Subsection 3.3.4 Blend Coal Analysis.

Test results for the Phase I Eagle Butte and Kentucky #9 parent coals were discussed at length in the Phase I Final Report (Boni et al., 1990).

FIGURE 7.3-33. - Ternary diagrams (Ca - Al - Si) of all ash particles containing sulfur produced by the combustion of the blended coal at 1700 K, 7% O₂.

FIGURE 7.3-34. - Ternary diagrams (Ca - Al - Si) of all ash particles containing sulfur produced by the combustion of the blended coal at 1700 K, 7% O_2 , and showing the composition of particles containing different amounts of sulfur.

7.3.4 Gravimelt 7A (Kentucky #9)

As part of the Phase II effort, ash formation during the combustion of two chemically cleaned coals was conducted. In this section, test results obtained during a study of a sample of chemically beneficiated Kentucky #9 coal, obtained directly from DOE/PETC, are presented. Cleaning was by the TRW molten caustic leach process known as Gravimelt, utilizing a 50:50 NaOH:KOH caustic mixture at a caustic to coal ratio of 2.5. The particular sample examined herein, containing approximately 0.5% ash, was denoted Gravimelt (sample) 7A by DOE/PETC.

Coal and ash analyses for Gravimelt 7A are presented in Table 7.3-21, and a more detailed ash analysis is presented in Table 7.3-22. An analysis of coal ash from a sample of Kentucky #9 examined previously at PSIT is presented for comparison (Boni et al., 1990). The overall ash level of this Kentucky #9 was 15.6% (dry basis); as this is a typical value for this coal, significant ash reduction was achieved in producing the 0.5% ash (dry basis) product. Two items are noteworthy in Table 7.3-22. First, the analysis performed by Coors Labs (ICP emission spectroscopy) was in good agreement with analyses performed by x-ray fluorescence and chemical fractionation at the University of North Dakota Energy and Environmental Research Center (UNDEERC) for all elements except sulfur and sodium. Silicon dominated the ash oxides, with aluminum, iron, and alkali all present in approximately equal quantities. Second, a comparison of the first three Gravimelt analyses with the Kentucky #9 ash analysis reveals fairly uniform removal of most inorganic species. Sodium and potassium fractions in the beneficiated coal ash are significantly higher than in the parent, although total alkali levels have decreased by a factor of approximately 3 to 5. The high relative alkali concentrations, however, suggest retention of alkali from the caustic leaching process. Higher titanium concentrations were also observed in the Gravimelt ash, suggesting that Ti was not as readily removed as other species. Titanium is one of the few minerals often present as very small ($0.2\ \mu\text{m}$) inclusions in bituminous coals (Allen and VanderSande, 1984; Palmer and Filby, 1984); it is conceivable that these were not extracted with high efficiency.

Mineral components of Gravimelt 7A are compared with those for the actual parent Kentucky #9 sample in Table 7.3-23. The distinction between "parent" Kentucky #9 coals needs to be emphasized - in Table 7.3-21, the Kentucky #9 sample from Phase I of this program is presented for comparison, whereas in Table 7.3-23 the actual parent Kentucky #9 sample analysis is shown. Ultimate and proximate analyses for the actual parent were unavailable at the time of publication of this report; hence, their omission from Table 7.3-21. Coal samples were analyzed by computer-controlled scanning electron microscopy, described in detail in Section 4 of this report and in the Phase I Final Report. Identifiable phases in the Gravimelt were dominated by quartz; illite, kaolinite, and pyrite were also observed in ca. 8% quantities. Unidentifiable phases (listed as unknowns in this report, and included in the other category in Table 7.3-23) included a range of aluminosilicates and silicates. Approximately 30% of the unknowns were rich in potassium chloride, indicative of potassium residue from the caustic leaching process.

TABLE 7.3-21. - Gravimelt sample 7A and 9C coal analysis (dry basis)

	Phase I Kentucky #9	Gravimelt 7A (Kentucky #9)
Volatile matter (dry, wt%)	37.6	24-26
Moisture (wt%)	8.3	17-47
Ultimate (wt%) (dry)		
C	65.4	79.4
H	4.7	3.5
N	1.8	1.8
S	3.9	0.7
O (difference)	8.6	14.0
Ash	15.6	0.6
Ash composition (wt%)		
SiO ₂	44.6	30.3
Al ₂ O ₃	20.6	11.3
TiO ₂	1.1	8.0
Fe ₂ O ₃	22.4	6.5
CaO	3.1	3.9
MgO	1.1	1.6
Na ₂ O	0.9	5.4
K ₂ O	2.6	7.5
SO ₃	4.7	25.5*
P ₂ O ₅	0.1	—
Chlorine (ppm of coal, wt)**	700	107
*By difference.		
**Galbraith Analytical Labs on as-received sample.		

TABLE 7.3-22. - Analysis of Gravimelt 7A coal
- SO₃ free basis -
- wt% -

Technique	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
Coors Labs/DOE	40.7	15.2	8.7	10.7	5.2	2.0	7.2	10.0
XRF*	34.8	14.3	14.5	9.0	4.7	0.7	13.4	7.5
Chem Fract*	40.5	15.8	15.8	-	6.1	2.2	8.7	10.9
CCSEM*	49	11	15	5	8	2	3	7
PSIT Ky#9	46.3	21.4	23.2	1.1	3.2	1.1	0.9	2.7
*Analysis by UNDEERC								

TABLE 7.3-23. - CCSEM mineral analysis of Gravimelt 7A
- wt% of mineral matter -

	Gravimelt 7A [†]	Gravimelt 7A [†] Modified ^{**}	KY#9 Parent *
Quartz	20.3	24.9	16
Kaolinite	5.7	7.0	6
Illite	7.6	9.3	7
Pyrite	7.0	8.6	62
Calcite	1.6	2.0	2
Mixed Silicates	9.7	11.9	2
Other [‡]	48.1	36.3	5
[†] CCSEM at UNDEERC *Analyzed under a separate program at UNDEERC **Excluding all particles containing > 10 atom percent Cl [‡] Includes unknowns			

Chlorine levels in the unknown category averaged 21%, with the largest of these unknown minerals (those greater than 10 μm) containing an average of 44 atom percent chlorine. Origins of such high levels of chlorine are uncertain at present. As inclusions with high chlorine (and K, Na) levels are expected to vaporize during combustion, the mineral CCSEM data were renormalized, excluding all minerals containing > 10 atom percent chlorine. These results, presented in the second column of Table 7.3-23, provide a more accurate representation of the mineralogy expected to contribute to the formation of residual (i.e., non-vaporized) ash particles.

Comparison of Gravimelt 7A CCSEM with the PSIT Kentucky #9 results in Table 7.3-23 suggests that quartz may have been removed less effectively than other major minerals. Illite to pyrite ratios were 1.4 in the Kentucky 9 and 1.1 in the Gravimelt, while illite to quartz ratios were 1.9 and 0.4, respectively. Lack of enrichment of silicon in the ash (Table 7.3-22) suggests, however, that *most* of the quartz had been removed from the coal.

Average chemical compositions for each major mineral class as determined by CCSEM are presented in Table 7.3-24 on a chlorine and phosphorous-free basis. These were calculated by adding the stoichiometric amount of oxygen was added to balance charge for each particle and summing individual elements for each category on an area-weighted basis. Chemical fractionation was also used to assess the forms of the inorganics within the Gravimelt 7A coal. As discussed in Subsection 3.3.2, successive extractions are performed with H_2O , $\text{NH}_4\text{OOCCH}_3$, and HCl to remove chlorides, salts of organic acids, and oxides and carbonates, respectively. Insoluble minerals such as pyrite or clays comprise the "remainder" category. As the results in Table 7.3-25 indicate, calcium and potassium were predominantly found in water-soluble forms, while silicon and aluminum were found in mineral form. Iron results reflect the split between pyrite and oxidized forms of iron, also observed by the CCSEM. Sodium results were highly unusual in their indication that most of the sodium was present in clay form. As subsequent discussion will indicate, this was contradictory both to expectation and to combustion testing results obtained at PSIT; for this reason, chemical fractionation of sodium was discounted, pending availability of additional evidence.

TABLE 7.3-24. - Average discrete mineral species composition - Gravimelt 7A
(atom percent)

	Na	Mg	Al	Si	S	K	Ca	Fe	Ti
Quartz	1	0	0	97	1	0	0	1	0
Kaolinite	0	0	44	52	0	1	1	1	1
Illite	1	0	31	53	1	11	1	1	1
Pyrite	0	1	1	1	74	0	1	21	1
Unknowns	10	4	10	23	16	15	11	7	4

TABLE 7.3-25. - Results of UNDEERC chemical fractionation of Gravimelt 7A coal

Element	% Removed by:			Remaining
	H ₂ O	NH ₄ OAc	HCl	
Na	6	2	1	91
Mg	47	5	10	38
Al	3	3	6	88
Si	1	2	2	95
K	80	6	1	13
Ca	75	15	10	0
Fe	3	1	74	22

Combustion experiments with this coal were conducted in the PSIT externally heated drop-tube reactor facility described previously. As-received coal samples (70% < 200 mesh) were dried overnight at 100°C prior to testing, thus reducing the water content below the original 50% value. Attempts were made at feeding the coal without pre-drying, but feeder line plugging prohibited this. Experiments were conducted at a wall temperature of 1773 K (corresponding to a gas temperature of approximately 1700 K, based upon measurements taken at the reactor outlet). Coal particle feed rates were maintained at 0.5 g/min in this study. Oxygen concentrations were maintained at 21% oxygen in nitrogen after it was determined that complete burnout was not occurring at lower oxygen levels.

To determine the extent of mineral interactions occurring during combustion, size distributions of the parent minerals and the combustion-generated ash were measured by CCSEM. A comparison of these size distributions is presented in Figure 7.3-35. Interestingly, the size distribution for the minerals in the parent Kentucky #9 coal, measured recently by UNDEERC in a separate program, was finer than those measured for the Phase I and Phase II Kentucky #9 samples of this program. Comparing the parent Kentucky #9 and the Gravimelt 7A sample, it is seen that the mineral size distribution did not change significantly despite a decrease in ash content to less than 1%.

From direct comparison of the measured mineral and ash distributions, some coalescence is apparent at the smaller end of the distribution. If the mineral distribution is replotted, however, minus those minerals possessing > 10% chlorine (large KCl and NaCl inclusions which are expected to vaporize during combustion), coalescence is evident throughout the entire distribution of sizes.

Interestingly, analysis of the chemical composition of the ash particle suggests that for quartz and illite, coalescence was primarily occurring between minerals of identical type (e.g., quartz with quartz, illite with illite). Recalling Table 7.3-23, 25% of the minerals were quartz and 9% were illite (chlorine-containing minerals excluded). As Table 7.3-26 indicates, 21.5% of the ash was silica, and 7% was potassium aluminosilicate. The

FIGURE 7.3-35. - CCSEM mineral and ash size distributions for Gravimelt 7A and parent Kentucky #9

TABLE 7.3-26. - Chemical composition of combustion-generated ash
Gravimelt 7A 1700 K. 21% O₂

Category	Wt% in Ash	(atom percent)								
		Na	Mg	Al	Si	S	K	Ca	Fe	Ti
Si	21.5	0	0	0	98	1	1	0	0	0
SiAl	9.6	1	0	44	47	1	3	1	1	1
SiAlK	7.2	1	0	34	52	2	7	0	2	1
Si-rich	5.6	1	0	11	77	3	4	1	1	2
Fe	4.1	0	0	0	2	0	1	0	95	1
Unknowns	39.6	1	2	15	33	8	3	12	7	18
Total	100.0	1	1	17	52	4	3	6	8	8

correspondence between chemical compositions and amounts of each of these ash species strongly suggests limited interaction among them. The increase in mass in the aluminosilicate category is likely indicative of the addition of some silica-rich particles to that class. Interactions among the other species present in the coal are more difficult to discern individually, as a result of low concentrations in the parent Gravimelt 7A coal.

Coalescence of quartz inclusions is also evident from a comparison of the CCSEM-derived SiO_2 mineral and ash particle size distributions, as shown in Figure 7.3-36. The solid curve at the left represents quartz minerals, which constituted 20 wt% of the ash (25% with chlorine-containing minerals excluded). The broken line at the right represents ash particles containing at least 90% silicon (oxygen-free basis). The uniform shift and constancy of composition suggest that most quartz minerals were coalescing with one another during combustion. Similar conclusions are drawn from an examination of illitic minerals and ash particles. As shown in Figure 7.3-37, an increase in average size was observed during combustion.

The degree of interaction of mineral species during combustion can also be determined from analysis of the chemical composition of individual particles, obtained from CCSEM analysis. By plotting this information on ternary diagrams, such that the sum of the three elements represented constitutes greater than some percentage x of the particle (x typically = 80%), changes in composition can be readily observed. Ternary plots are presented on an oxygen free, normalized atom percent basis.

In Figure 7.3-38 (a), a ternary K-Al-Si diagram for Gravimelt 7A gives an indication of the range of compositions present in K-Al-Si rich minerals. Clustering near the Si apex

FIGURE 7.3-36. - CCSEM quartz mineral and silica ash particle size distributions for Gravimelt 7A.

FIGURE 7.3-37. - Illite mineral and ash particle size distributions by CCSEM.

represents quartz, clustering along the Al-Si axis represents kaolinite, and clustering near the K=10 line represents illite. Comparison with Figure 7.3-38 (b), a ternary K-Al-Si diagram for the combustion-generated ash, suggests that some coalescence has occurred between these mineral groups. The retention of clusters near the Si apex and K=10 line suggest, however, that most illite and quartz minerals did not interact with other aluminosilicates present in this coal. These plots also indicate a lack of potassium uptake by these minerals, despite the presence of large amounts of water-extractable potassium (KCl; cf. Table 7.3-25) in the coal. In Figure 7.3-38 (a), a few particles containing 10 to 15% potassium are observed; the same is true of the ash particles in Figure 7.3-38 (b). The average potassium concentration of minerals plotted in Figure 7.3-38 (a) is 3%; in Figure 7.3-38 (b), the average potassium concentration is also 3%. Clearly, no increase in potassium level occurred.

Analysis of the chemical composition of specific mineral and ash types generates similar conclusions. In Figure 7.3-39, K-Al-Si ternary mineral and ash diagrams for illitic species confirm a lack of potassium uptake. Potassium levels in fact decreased, from 10% in the illite minerals to 7% in the illite-derived ash particles, suggesting some (limited; recall previous discussion) interaction with aluminosilicates. Figure 7.3-40 presents the same information for kaolinite-type minerals and ash particles. Some spreading of the range of observed Al-Si compositions is seen, suggestive of coalescence between aluminosilicate particles.

(a) Gravimelt 7A minerals

(b) PSIT combustion ash

FIGURE 7.3-38. - K-Al-Si Ternary composition diagram for Gravimelt 7A, all particles 0.5 to 80 μm , ≥ 80 atom percent K + Al + Si.

(a) Gravimelt 7A Minerals

(b) PSIT Combustion-generated Ash

FIGURE 7.3-39. - K-Al-Si Ternary composition diagram for Gravimelt 7A illite-type particles $0.5 \mu\text{m} < d_p \leq 80 \mu\text{m}$, $K + Al + Si > 80\%$.

(a) Minerals

(b) Ash

FIGURE 7.3-40. - K-Al-Si Ternary composition diagram for Gravimelt 7A kaolinite-type particles. $0.5 \mu\text{m} < d_p \leq 80 \mu\text{m}$, $K + Al + Si > 80\%$.

For comparative purposes, size distributions of "unknown" mineral and ash particles are presented in Figure 7.3-41. Because the composition of the minerals is different from that of the ash, mechanistic information cannot be inferred for this class of particles (see Tables 7.3-24 and 7.3-26). Note, however, that the exclusion of chlorine-rich particles causes a significant decrease in the average size of the minerals, consistent with the observation of large ($d_p > 10 \mu\text{m}$) potassium chloride crystals in CCSEM images.

FIGURE 7.3-41. - Size distributions for Gravimelt 7A mineral and ash particles which do not correspond to a crystalline mineral category.

7.3.4.1 Fate of iron during ash formation

In formation of slag deposits in utility boilers, iron often functions as a fluxing agent, reducing the viscosity of slags and allowing them to sinter more rapidly. It was therefore important to determine whether iron was interacting with aluminosilicate minerals to form low viscosity iron-aluminosilicate ash particle during combustion of Gravimelt 7A.

Table 7.3-27 compares the fractions of total iron in various mineral and ash categories. Mineral-bound iron was evenly divided amongst pyrite, iron oxide, oxidized pyrrhotite, and various non-classifiable phases in the parent coal. Recalling the chemical fractionation results of Table 7.3-25, most of the iron within the coal was present in mineral forms; examination of mineral iron only therefore provides a good representation of the overall distribution of iron in the coal. As Table 7.3-27 also shows, this distribution did not

TABLE 7.3-27. - Distribution of iron in Gravimelt 7A minerals

Phase	Wt% of Minerals	Percentage of Total Mineral Iron	Percentage of Iron in Various Ash Phases
Pyrite	7.0	20	0
Iron Oxide	2.7	24	37
Oxidized Pyrrhotite	2.4	20	22
Iron Aluminosilicate	0	0	2
Iron Silicate	0	0	1
Unknown Phases	41.5	28	34

shift significantly toward aluminosilicate species upon combustion of Gravimelt 7A. Sixty-nine percent of the iron in the ash is present in oxidized forms, with only 3% in clearly identifiable aluminosilicates. As it is possible that a portion of the coal iron is residing in the submicron fume (which has not been characterized), an overall iron balance cannot be closed. Nevertheless, one can conclude that virtually no iron-aluminosilicate phases formed during combustion.

The same conclusion can be drawn from the Fe-Al-Si ternary diagrams in Figure 7.3-42. In part (a) of the figure, a lack of iron aluminosilicate minerals in the coal is clearly evident. In part (b), the formation of a few iron-containing aluminosilicates is evident; these represent particles in the "unknown" category of Table 7.3-27. Most particles, however, have remained at their initial 1 to 2% iron levels, indicating little formation of iron aluminosilicates during combustion.

7.3.4.2 Fate of calcium during ash formation

Phase 1 of the PSIT study utilizing seven well-characterized U.S. coals indicated that the formation of calcium aluminosilicate ash particles significantly increased the stickiness of the ash (Boni et al., 1990). This suggests that inertial deposition of sticky ash particles - slagging predominantly - could be decreased if calcium aluminosilicate formation did not occur. To assess this possibility for Gravimelt 7A, CCSEM chemical composition data were again used to generate ternary composition diagrams. In part (a) of Figure 7.3-43, a Ca-Al-Si diagram for the coal minerals indicated a lack of calcium aluminosilicates in the Gravimelt coal. In Figure 7.3-43 (b), a scenario similar to iron is observed - extremely limited interaction between calcium and aluminosilicate minerals in the final ash.

(a) Minerals in Gravimelt 7A

(b) PSIT combustion-generated ash, 1700 K, 21% O₂/N₂

FIGURE 7.3-42. - Gravimelt 7A Fe-Al-Si Ternary composition diagram,
0.5 < d_p ≤ 80 μm, Fe + Al + Si > 80 atom percent.

(a) Minerals in Gravimelt 7A

(b) PSIT combustion-generated ash, 1700 K, 21% O_2/N_2

FIGURE 7.3-43. - Gravimelt 7A Ca-Al-Si Ternary composition diagram,
 $0.5 < d_p, \leq 80 \mu m$, $Ca + Al + Si > 80$ atom percent.

This lack of interaction was not inherently obvious from an examination of the coal inorganic distribution. As the chemical fractionation results of Table 7.3-25 indicated, most of the calcium was present in highly dispersed, water and acetate soluble forms. This distribution, typical of western coals such as Eagle Butte from the Powder River basin, tends to promote formation of calcium-rich aluminosilicate ash particles. Despite the presence of dispersed calcium, Ca-Al-Si formation was not observed for the Gravimelt. Why? The answer lies in the relative amounts of calcium and aluminosilicates present in the coal. Ca/Si ratio can be used as a crude guideline; for Gravimelt 7A it was 1/6, while it was nearly 1/1 for Eagle Butte. Absolute amounts were also significantly lower in the Gravimelt as a result of a total ash level of only 0.5%. Such low absolute ash levels greatly increase the diffusion or coalescence distance for species within a coal particle, greatly decreasing the potential for species interaction during combustion. This coupled with the low amount of calcium per available aluminosilicate severely limited any interaction between species despite the presence of highly dispersed calcium.

7.3.4.3 Fate of sodium during ash formation

Sodium is primarily of concern in combustion systems because of its volatility, allowing it to escape the combustion chamber and react with metal surfaces or recondense downstream as chloride or hydroxide. In either case, corrosive sodium sulfate will result. It is therefore desirable to minimize the vaporization of sodium from coal during combustion. Research has shown that coals with high concentrations of silicates may retain a portion of the sodium as sodium aluminosilicate; this possibility was explored in combustion testing of Gravimelt 7A.

As mentioned previously in this report, chemical fractionation suggested that most of the sodium was bound to clays within the Gravimelt 7A matrix. This surprising result was not consistent with CCSEM analysis of the minerals, as shown in Figure 7.3-44. In Figure 7.3-44 (a), a ternary Na-K-Cl diagram shows the presence of mixed potassium/sodium chloride crystals throughout the coal. A lack of sodium in corresponding aluminosilicate minerals is clearly shown by Figure 7.3-44 (b). This would suggest that most of the sodium would vaporize during combustion; little is expected in aluminosilicate form.

Examination of ash particle chemical composition in Figure 7.3-45 supports this hypothesis. In both part (a), an Na-Al-Si ternary composition diagram for all ash particles, and part (b), highlighting those of the kaolinite category, no interaction between sodium and aluminosilicates is seen. Overall sodium levels decreased from 3% in the coal minerals to 0.5% in the ash, suggestive of sodium vaporization. If this is indeed the case, the submicron fume will be enriched in sodium and chlorine, leading to potentially severe fouling problems.

7.3.4.4 Fate of titanium during ash formation

As a percentage of the ash, titanium levels in the Gravimelt 7A were significantly higher than those typically encountered in "raw" pulverized coal. As shown in Figure 7.3.46 (a), the titanium was initially present in less than 5% concentrations in aluminosilicate ash

(a) $\text{Na} + \text{K} + \text{Cl} \geq 40\%$

(b) $\text{Na} + \text{Al} + \text{Si} \geq 80\%$

FIGURE 7.3-44. - Na Ternary composition diagrams for Gravimelt 7A coal minerals,
 $0.5 < d_p \leq 80 \mu\text{m}$.

(a) All ash particles

(b) Kaolinite-type ash particles

FIGURE 7.3-45. - Na-Al-Si Ternary diagrams for Gravimelt 7A combustion-generated ash. $0.5 < d_p \leq 80 \mu\text{m}$, $\text{Na} + \text{Al} + \text{Si} \geq 80$ atom percent.

(a) $\text{Ti-Al-Si} \geq 70\%$, minerals

(b) $\text{Ti-Fe-Ca} \geq 40\%$, minerals

(c) $\text{Ti-Al-Si} \geq 80\%$, ash

FIGURE 7.3-46. - Ternary diagrams for Gravimelt 7A titanium minerals and ash particles, $0.5 < d_p \leq 80 \mu\text{m}$.

particles. As shown in Figure 7.3-46 (b), rutile minerals were occasionally observed, as indicated by the points near the titanium apex. Subsequent to combustion, there is apparent interaction between titanium and aluminosilicates (Figure 7.3-46 (c)). Particles with a wide range of compositions are formed, although the bulk of the particles (by mass and number) contain less than 10% titanium.

7.3.4.5 Formation of Submicron Ash

Limited experiments to determine the overall ash particle size distribution from Gravimelt 7A under selected combustion conditions were also conducted. In some samples, as-received coal samples - approximately 70% < 200 Mesh, as estimated by DOE/PETC - were used, while in others, the coal was sieved to a top size of 90 μm . Combustion was carried out at a reactor wall temperature of 1773 K (1500°C), corresponding to a gas temperature of 1700 K. Oxygen concentrations were maintained at either 7 or 21%. Particle size distributions were measured with a Pollution Control Systems Corporation Mark III Cascade Impactor plus backup filter. Greased collection plates were employed to minimize particle bounce.

Three different combinations of coal particle size and oxygen level were used in these experiments. As the size distributions in Figure 7.3-47 show, little difference was observed among them. In all three cases, over 50 mass% of the ash was collected on the top stage of the impactor, which has a nominal cutoff diameter of 8 μm . Slightly larger amounts were collected when the as-received size of coal was burned. This was not surprising for this particular fuel. Because of the extensive treatment undergone by Gravimelt samples in the beneficiation process, a fairly uniform product is expected to result. Large coal particles should therefore have the same fraction of ash as small coal particles (0.5% for 7A). By including larger coal particles in the feed, larger ash particles would therefore result.

To obtain an accurate size distribution from the cascade impactor data, the top size on stage 1 should be measured and the data subsequently inverted using one of the many inversion algorithms developed for this purpose. This was not necessary here, however, as the goal of these tests was to determine the split between submicron fume and larger residual ash particles. Taking stage 7 plus the filter as defining the fume (based on prior observation, as well as a diameter cutoff of < 0.25 μm), 18 to 20% of the inorganic species resided in the submicron fume for the coal sizes and combustion conditions considered. This fraction is significantly greater than the 0.5 to 2% generally observed in previous studies with non-cleaned coals at this facility (1). Recalling that sodium, potassium, and chlorine concentrations were depleted in the ash relative to their concentration in the coal, one reaches the conclusion that a fume rich in sodium and potassium chloride results from combustion of Gravimelt 7A. This was indeed the case, as indicated by testing of this coal at M.I.T. and UA (Subsections 6.5.5.2 and 5.4.1.3 of this report).

FIGURE 7.3-47. - Cascade impactor size distribution for combustion-generated ash. Gravimelt 7A, 1700 K, oxygen and coal particle size as indicated

7.3.4.6 Summary - Gravimelt 7A Study

Examination of the Gravimelt 7A coal inorganic composition indicated that all minerals had been reduced to very low concentrations, although relative sodium and potassium levels had increased (as a fraction of the ash) during the caustic leaching process. Titanium levels were also observed to increase, but the reasons for this are less clear. There has been general speculation that titanium has been leached from the steel processing vessels used in preparing the Gravimelt; it is more plausible, however, that the increase in relative Ti concentration arises from retention of fine rutile crystals in the coal. Further analysis utilizing STEM of both the parent and the Gravimelt coal would resolve this. Despite a significant decrease in ash content, overall mineral size distributions for the coal remained unchanged.

Combustion experiments indicated that coalescence did occur between minerals, but was not extensive in scope. Little interaction was noted between mineral species of different types, with the exception of titanium, again possibly due to the presence of small rutile inclusions dispersed throughout the coal. Neither calcium, sodium, potassium, nor iron were

observed to interact with aluminosilicate minerals to any significant extent. Quartz inclusions were observed to interact primarily with other quartz inclusions, as indicated by the lack of a decrease in quartz concentration during the mineral to ash transition. Measurement of the submicron fume showed that a significant fraction of the remaining inorganic species vaporized, producing a fume rich in alkali metals.

Further discussion of Gravimelt 7A is presented in:

Subsection 7.7	PSIT Stickiness Testing
Subsection 6.5.5.2	UA Burns 52 and 53 - Gravimelt 7A
Subsection 5.4.1.3	MIT Chemical Analysis of Submicron Ash
Subsection 3.3.2	Coal Analysis - Gravimelt 7A and 9C

See also the related discussion of Gravimelt 9C (Pittsburgh #8 bituminous coal parent) in Subsection 7.3.5 of this report.

7.3.5 Gravimelt 9C (Pittsburgh #8)

During the PSIT Phase II effort, a second sample of Gravimelt coal was also studied. This sample, denoted number 9C, was derived from a Pittsburgh #8 bituminous coal, and cleaned using only sodium hydroxide as the caustic solution. An analysis of the coal and the ash composition for the Gravimelt 9C coal is presented in Table 7.3-28. The total ash content of the coal calculated from the inorganic analysis was 0.2%. Silica was the major inorganic oxide in the ash, as indicated by x-ray fluorescence analysis. Little enrichment was noted among iron, calcium, magnesium, and aluminum relative to typical ash chemistries for bituminous coals, suggesting that all of these elements were removed to a significant extent. High titania levels of 15% suggested that Ti was not as readily removed as other species. Titanium is one of the few minerals generally present in high concentration as submicron inclusions in bituminous coals (Allen and VanderSande, 1984; Palmer and Filby, 1984); it is conceivable that these were not extracted with as high efficiency as the other minerals. High chromium levels in the ash (7500 ppm) suggested that it was also ineffectively removed relative to the other inorganic species. Sodium levels in the ash were also elevated as compared to a "typical" bituminous coal. This is suggestive of retention of alkali from the beneficiation process.

Chemical fractionation of the coal inorganics was also performed to assess their chemical form within the coal. In this procedure, successive extractions are performed with H_2O , $NH_4OOC_2H_3$, and HCl to remove chlorides, salts of organic acids, and oxides and carbonates, respectively (Benson and Holm, 1985). Insoluble clays and pyrite typically constitute the remainder. As Table 7.3-29 indicates, sodium, potassium, and chlorine were 100% water-extractable, indicating a lack of mineral forms of these species. Magnesium, aluminum, and silicon were retained in the coal, a likely indication of the presence of small quantities of clay. Calcium was most probably present as the carbonate (calcite). The non-existence of "remaining" or non-extractable iron indicates a lack of pyritic iron detectable by this technique.

TABLE 7.3-28. - Gravimelt sample 9C coal analysis (dry basis)

	Gravimelt 9C (Pittsburgh #8)
Volatile matter (dry, wt%)	20.5
Moisture (wt%)	6-46
Ultimate (wt%) (dry)	
C	79.7
H	3.8
N	1.6
S	0.4
O (difference)	14.1
Ash	0.4
Ash composition (wt%)	
SiO ₂	29.9
Al ₂ O ₃	10.6
TiO ₂	10.9
Fe ₂ O ₃	12.6
CaO	2.9
MgO	2.9
Na ₂ O	5.1
K ₂ O	2.9
SO ₃	23.4*
P ₂ O ₅	—
Chlorine (ppm of coal, wt)	< 43**
Mn = 428 ppm of ash Cr = 7500 ppm of ash *By difference. **Galbraith Analytical Labs on as-received sample.	

CCSEM analysis of the minerals, however, suggests that some pyritic iron did remain within the coal. This is shown in Table 7.3-30. Quartz was the other major identifiable mineral remaining in the coal after beneficiation, with moderate amounts of alumina, silica-rich phases, and aluminosilicate clays observed. Unknown phases (i.e., those not corresponding to one of the 32 common coal minerals categorized by UNDEERC CCSEM analysis) constituted 55 wt% of the minerals. Many of the "unknown" particles, however, were primarily chlorine, often containing potassium and sulfur as shown in the CCSEM

TABLE 7.3-29. - Chemical fractionation of Gravimelt 9C coal

Element	ppm of mf Coal	Removed by H ₂ O (%)	Removed by NH ₄ O Ac (%)	Removed by HCl (%)	Remaining (%)
Na	220	100	0	0	0
Mg	14	0	0	0	100
Al	100	30	0	0	70
Si	240	27	0	0	73
Cl	53	100	0	0	0
K	73	100	0	0	0
Ca	32	78	0	22	0
Fe	140	10	0	90	0

TABLE 7.3-30. - CCSEM mineral analysis of Gravimelt 9C
- wt% of mineral matter -

	Pitts #8 Minerals	Grav 9C Minerals	Modified Analysis*
Quartz	10.8	20.1	27.5
Alumina	0.0	4.7	6.5
Kaolinite	12.6	1.3	1.7
Illite	5.8	1.2	1.6
Pyrite	54.7	11.5	15.7
Si-Rich	0.6	6.3	8.7
Other**	15.5	54.9	38.3
*Particles containing ≤ 10 atom percent Cl only.			
**Includes unknowns.			

ternary diagram of Figure 7.3-48. Removing these from the analysis results in the modified mineral distribution shown in the third column of Table 7.3-30. The low chlorine levels indicated by XRF (53 ppm of the coal, $\approx 2.5\%$ of the ash) suggest that the high-Cl particles observed by CCSEM may have been an artifact. Note that CCSEM analysis of this coal is particularly difficult, given the low loading and small size of the few discrete minerals remaining after beneficiation.

FIGURE 7.3-48. - CCSEM mineral analysis of Gravimelt 9C (Pittsburgh #8), showing all particles containing greater than 60 atom percent K+Cl+S on an oxygen-free basis.

Mineral size distributions determined by CCSEM for the parent Pittsburgh #8, analyzed by UNDEERC as part of a separate program, are presented in Table 7.3-31. Mineral size distributions for the Gravimelt 9C cleaned coal are given in Table 7.3-32. In the Gravimelt sample, the majority of the observed minerals were $< 10 \mu\text{m}$ in size, confirming removal of large mineral species during coal cleaning. Average atomic chemical compositions for each major mineral class as determined by CCSEM are presented in Table 7.3-33. These were calculated by adding the stoichiometric amount of oxygen to the CCSEM atomic elemental analysis to balance charge as necessary for each particle. Individual elements were then summed for each category and renormalized to yield the final elemental atom fractions.

Combustion experiments with the Gravimelt 9C coal were conducted in the PSIT externally heated drop tube reactor facility. Pittsburgh #8 parent coal was not provided to this program; therefore, no experiments were conducted with this fuel. Gravimelt 9C coal samples were sieved to 100% $< 90 \mu\text{m}$ prior to testing to ensure that complete combustion would occur in 7% oxygen atmosphere at gas temperatures of 1700 to 1725 K (corresponding to wall temperatures of 1773 K = 1500°C). Gas flow rates were maintained at 21.2 slpm in the 9 cm diameter 1.3m long reactor for these experiments.

Particle size distributions of coal minerals and ash particles generated during these combustion experiments were determined by CCSEM and plotted in Figure 7.3-49. The mineral size distribution for the parent Pittsburgh #8 is also plotted for comparison. Unlike the Gravimelt 7A (Kentucky #9) coal, beneficiation of the Pittsburgh #8 resulted in a finer

TABLE 7.3-31. - CCSEM mineral size distributions
Parent Pittsburgh #8 (area % of minerals)

	1.0 to 2.2 μm	2.2 to 4.6 μm	4.6 to 10 μm	10 to 22 μm	> 22 μm	wt% in Mineral Matter
Quartz	28	41	23	7	1	10.8
Pyrite	19	21	23	21	17	54.7
Kaolinite	32	41	15	10	2	12.6
Illite	39	36	15	10	1	5.8
Totals	29.4	26.2	19.4	15.2	11.5	100.0

TABLE 7.3-32. - CCSEM mineral size distributions
Gravimelt 9C (area % of minerals)

	1.0 to 2.2 μm	2.2 to 4.6 μm	4.6 to 10 μm	14 to 22 μm	> 22 μm	wt% in Mineral Matter
Quartz	17	42	27	14	0	20.1
Alumina	8	56	36	0	0	4.7
Pyrite	73	27	0	0	0	11.5
Si-Rich	8	21	45	25	0	6.3
Fe-Oxide	13	44	44	0	0	2.7
Totals	27.0	34.9	32.8	5.3	0	100.0

TABLE 7.3-33. - Gravimelt 9C average discrete mineral composition
(CCSEM, atom percent, O-free basis)

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Ti
Quartz	0	0	0	96	0	1	1	0	1	1	0
Alumina	0	0	95	0	0	1	1	1	1	0	1
Pyrite	0	0	0	0	0	75	1	0	0	23	0
Si-Rich	2	1	7	81	0	0	1	1	3	3	1
Unknowns	1	1	4	10	4	2	67	1	2	6	2
Overall	1	1	8	28	2	16	28	1	2	9	4
Overall Mod*	0	0	9	37	3	27	1	1	2	15	6
*Particles containing ≤ 10 atom percent Cl only.

FIGURE 7.3-49. - Mineral and ash size distributions for Gravimelt 9C.

mineral distribution in the Gravimelt sample. Comparing the uncorrected mineral and ash size distributions suggests that significant coalescence of inorganics occurred during combustion, as the fraction greater than $8\ \mu\text{m}$ is much greater for the ash. If both distributions are modified by eliminating all particles containing greater than 10 atom percent chlorine, however, the extent of coalescence is much less as shown in Figure 7.3-49. Because of the uncertainty in chlorine analysis (i.e., the apparent large difference between XRF and CCSEM reported levels), the modified curves are considered more accurate.

In Figure 7.3-50, the quartz mineral size distribution measured by CCSEM is compared with the SiO_2 CCSEM ash particle size distribution. Comparison with the quartz mineral distribution in the parent Pittsburgh #8 demonstrates a shift to larger sizes, suggesting that the finest minerals were removed by beneficiation. Examining the ash relative to the 9C minerals, a slight increase in particles greater than $8\ \mu\text{m}$ is observed. This suggests that very limited coalescence of quartz minerals may be occurring. Given the low (0.20%) ash content of this coal, little coalescence was anticipated.

The chemical composition of the combustion generated ash for Gravimelt 9C measured by CCSEM is given in Table 7.3-34. Chemical composition information is presented for "whole" particle samples (i.e. not cross-sectioned) unless otherwise noted. The overall compositions reported at the bottom of Table 7.3-34, modified to eliminate chlorine-rich particles, differ from the overall mineral compositions reported in Table 7.3-33 in several areas. First, sulfur levels are reduced in the ash, as expected given the volatility of the element under combustion conditions. Second, iron levels are decreased in the ash

FIGURE 7.3-50. - CCSEM quartz mineral and ash size distributions for Gravimelt 9C.

TABLE 7.3-34. - Chemical composition of combustion-generated Gravimelt 9C ash
(cross-sectioned sample)

Category	wt% in Ash	Atom Percent										
		Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Ti
Si	20.7	0	0	0	95	0	1	1	1	0	1	1
Ti	6.7	0	0	2	3	1	1	2	2	4	7	78
AlSi	4.2	1	6	41	49	0	1	2	4	1	1	1
KAlSi	4.6	1	0	31	52	0	1	1	8	1	2	2
Si-Rich	3.2	1	0	5	76	0	2	2	5	1	1	5
Unknowns	54.2	1	2	9	22	2	11	10	9	7	8	20
Unknowns, Mod ⁺	-	1	1	11	27	2	7	4	6	8	8	25
Overall	100.0	1	1	14	53	1	1	1	2	4	6	15
Overall, X-S	100.0	1	1	10	42	1	7	6	6	6	5	15
Overall, Mod ⁺	-	1	1	11	49	1	4	2	4	6	4	16

⁺ Particles containing ≤ 10 atom percent Cl only.

relative to the coal minerals. Third, titanium levels are increased in the ash relative to the coal minerals. The reduction in iron levels may be the result of dilution by organically bound species which add to the ash, while the apparent increase in titania may result from addition of submicron titania inclusions too small to be observed by CCSEM analysis of the coal. Both of these proposed mechanisms are speculative, as detailed characterization of the submicron minerals by a technique such as STEM (scanning transmission electron microscopy) would be required to address the issues.

Distributions were measured on samples which were cast in epoxy and cross-sectioned as well as on whole particle samples attached to double-sided adhesive tape. Comparison of the two provides a means for determining whether surface enrichment of any particular element exists, as the whole particle technique provides information on the outer approximately 1 μm of a particle. For this sample, silica-rich particles appear to be the only ones significantly surface enriched as shown in Table 7.3-35. This results in the slightly higher (53 versus 42 atom percent) silicon concentrations in the surface ash are reported at the bottom of Table 7.3-34.

TABLE 7.3-35. - Comparison of surface and cross-sectional CCSEM
- Gravimelt 9C Ash -

Category	X-S* Percent	Surface Volume Percent	Mineral** (X-S)
Si	21.6	32.4	23.3
Ti	3.8	3.7	0.1
Al Si	4.4	6.1	1.5
KAl Si	4.9	1.9	1.4
Si-rich	3.4	5.5	7.3
Unknown	55.4	40.5	44.4
*X-S area equivalent to volume; surface analysis values were converted to volume			
**N.B. - area percent; values in Table 7.3-31 are weight percent.			

Although most minerals did not coalesce to a significant extent for this fuel (cf. Figures 7.3-49, 7.3-50), extensive titanium-aluminosilicate interactions were observed. This can be seen in the series of ternary diagrams in Figures 7.3-51 through 7.3-53. In Figure 7.3-51, all coal minerals containing greater than 50 atom% Ti+Al+Si are seen to have low titanium content. When ash particles containing greater than 80% Ti+Al+Si are considered, an increase in titanium concentrations is observed. Broadening the categorization

FIGURE 7.3-51. - CCSEM Ti-Al-Si ternary for Gravimelt 9C, showing all minerals containing ≥ 50 atom% Ti+Al+Si.

to include all ash particles containing greater than 50 atom% Ti+Al+Si reveals a much larger number of titanium containing particles, as shown in Figure 7.3-52 (b). The difference in the number of particles observed in Figure 7.3-52 (b) versus 7.3-52 (a) indicates a high concentration of titanium aluminosilicates containing 20 to 50% of other species. Similar conclusions can be drawn from analysis of the cross-sectioned Gravimelt 9C ash sample in Figure 7.3-52. Comparison with the whole-particle or surface-sensitive CCSEM results in Figure 7.3-53 indicates titanium enrichment on the particle surface relative to the core, as discussed previously in this section. Examination of ternary diagrams for other species including K-Al-Si did not reveal any significant interaction during combustion.

For a beneficiated fuel with the low ash levels and high alkali content of the Gravimelt 9C, vapor-driven deposition (i.e. fouling) is expected to be a more serious problem than inertially-driven deposition of sticky ash particles in a boiler radiant zone. The high levels of submicron ash measured during laboratory combustion of this coal, suggestive of vaporization and recondensation of the volatile alkali (as well as refractory species; Graham, 1991) indicate this may be a concern. Two percent or less of the ash present in submicron size ranges is typical of bituminous coals examined under this program; slightly more than 10% was measured for this coal as shown in Figure 7.3-54. This level was slightly less than those measured for the Gravimelt 7A coal at PSIT (see Figure 7.3-47). The composition of the Gravimelt 9C submicron ash was greater than 80% sodium by weigh (oxygen-free basis) based upon measurements made at MIT (Subsection 5.4.1.3).

FIGURE 7.3-52. - CCSEM Ti-Al-Si ternary for ash particles generated during combustion of Gravimelt 9C ($< 90 \mu\text{m}$), 1500°C 7% O_2 . (a) $\text{Ti} + \text{Al} + \text{Si} \geq 80 \text{ atom\%}$; (b) $\text{Ti} + \text{Al} + \text{Si} \geq 50 \text{ atom\%}$. Surface CCSEM analysis.

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FIGURE 7.3-53. - CCSEM Ti-Al-Si ternary for ash particles generated during combustion of Gravimelt 9C ($< 90 \mu\text{m}$), 1500°C 7% O_2 . (a) $\text{Ti} + \text{Al} + \text{Si} \geq 80 \text{ atom\%}$; (b) $\text{Ti} + \text{Al} + \text{Si} \geq 50 \text{ atom\%}$. Cross-sectional analysis.

FIGURE 7.3-54. - Cascade impactor mass distribution obtained from combustion of Gravimelt 9C at a gas temperature of 1700 K.

In summary, examination of a 0.2% ash chemically beneficiated sample of Pittsburgh #8 coal and its combustion products revealed the following:

- coal low in ash, but ash contained high levels of alkali, sulfur.
- coal ash contained 15% titanium by weight, indicating less effective titanium removal relative to other minerals.
- chemical fractionation reveals that most elements were removed by extraction; retained Al and Si indicate some aluminosilicate minerals remained.
- fine mineral distribution; 95% less than 10 μm according to CCSEM.
- combustion ash particle surfaces slightly enriched in silicon relative to cross-sectioned sample (CCSEM analysis); no other elements enriched.
- extensive titanium aluminosilicate formation observed in combustion ash.
- submicron ash represents over 10 wt% of total combustion ash, suggestive of more extensive inorganic vaporization than typically noted for a bituminous coal.

7.3.6 Submicron Fume Formation - Summary

The chemical composition of the submicron fume generated during combustion of the program coals was examined in detail by researchers at the University of Arizona and, to a lesser extent, at MIT. Because of these efforts, work at PSIT did not address the composition of the submicron ash. Measurements were made with a cascade impactor for all

program coals, however, to determine the fraction of the coal ash appearing in the submicron size range.

In Tables 7.3-36 through 7.3-41, the measurements obtained for Phase I coals and reported in the Phase I Final Report are reproduced. Temperatures reported in these tables refer to either peak flame temperature for the self-sustained reactor (UA) or bulk gas temperatures for the drop-tube reactors (PSIT, MIT). In general, at combustion conditions comparable to a stoichiometric ratio of 1.2, less than 1% of the ash was collected in the submicron size range during the combustion of bituminous coals at PSIT and UA. For the lignite and sub-bituminous coals, 1 to 2% of the ash was collected in the submicron size range. This was attributed to the high fraction of organically associated inorganic species in these coals. At MIT and PSIT under higher oxygen conditions, a greater percentage of ash was present in the submicron range. This fraction was seen to increase with increasing oxygen level in experiments at MIT. If vaporization is assumed to be the underlying mechanism responsible for the bulk of this material (Subsection 5.3.2 of this report), then the increase in particle combustion temperatures with increasing O₂ concentrations would explain the observed trend.

For the Phase II beneficiated coal samples, shown in Tables 7.3-42 through 7.3-46, a similar dependence of the fraction of ash vaporized on the combustion oxygen level was observed. It is interesting to note that at all facilities, the fraction of ash present in the submicron mode was greater for the beneficiated coals than for any of the "raw" coals examined during Phase I. This can be attributed to the removal of high mineral-content coal particles by beneficiation, causing the organically associated material (or volatile inorganics) to an increase as a fraction of the total ash content. Thus, the fraction vaporizing would be expected to increase. Reducing the ash content also reduces the amount of fly ash available to act as a sink for vaporized species, particularly alkali species. This too would increase the fraction of ash present in the submicron range. In the case of the chemically beneficiated coals, reducing the ash content reduces the mineral content significantly, thus decreasing the mass of material available to coalesce with the volatile species within a burning char particle. Again, this would increase the fraction of ash able to vaporize and appear in the submicron size range.

Examining the coals individually, Table 7.3-42 presents fume levels for the Loy Yang 2301 and Loy Yang 1953 coals. Fume levels were lower for the LY 1953 at all three facilities. As discussed previously, reduced vaporization was expected relative to the LY 2301 because of decreased sodium/aluminosilicate ratios in the LY 1953. Both Loy Yang samples are rich in sodium, with the resultant submicron fume being highly enriched in sodium as a result. Recalling the discussion in Subsection 6.6.2.4.2, it is the fraction of sodium in the coal relative to the amount of aluminosilicates present that determines the amount of alkali residing in the submicron fume. Hence, because the Loy Yang 1953 has a greater amount of aluminosilicates per mass of sodium, reduced vaporization was observed.

Table 7.3-43 presents results obtained during combustion of the Illinois #6 SOAP coal. Values higher than the <1% observed for "raw" bituminous coals were reported at

TABLE 7.3-36. - Fume formation - Kentucky #9

Facility	Coal Size	Gas Conditions	S.R.	Wt% < 0.5 μm
MIT	63/75 μm	1650 K, 20% O ₂	7-20	6
U. Arizona	70% < 74 μm	1700 K*	1.2	1
PSIT	70% < 74 μm	1500 K, 30% O ₂	6-10	8
*Peak flame temperature, self-sustained combustion.				

TABLE 7.3-37. - Fume formation - Kentucky #11 bituminous

Facility	Coal Size	Gas Conditions	S.R.	Wt% < 0.5 μm
U. Arizona	70% < 74 μm	1600 K	1.2	< 1
PSIT	70% < 74 μm	1500 K, 7% O ₂	1.5-2	7

TABLE 7.3-38. - Fume formation - Upper Freeport bituminous

Facility	Coal Size	Gas Conditions	S.R.	Wt% < 0.5 μm
PSIT	70% < 74 μm	1500 K, 30% O ₂	6-10	< 1
U. Arizona	70% < 74 μm	1600 K	1.2	< 1

TABLE 7.3-39. - Fume formation - Eagle Butte sub-bituminous

Facility	Coal Size	Gas Conditions	S.R.	Wt% < 0.5 μm
MIT	63/75 μm	1650 K, 20% O ₂	7-20	12
PSIT	70% < 74 μm	1500 K, 21% O ₂	4.5-6	4
PSIT	70% < 74 μm	1500 K, 7% O ₂	1.5-2	1
U. Arizona	70% < 74 μm	1700 K*	1.2	2
*Flame temperature, self-sustained combustion.				

TABLE 7.3-40. - Fume formation - Beulah lignite

Facility	Coal Size	Gas Conditions	S.R.	Wt% < 0.5 μ m
MIT	63/75 μ m	1650 K, 20% O ₂	7-20	11
PSIT	70% < 74 μ m	1500 K, 21% O ₂	4.5-6	9
PSIT	70% < 74 μ m	1500 K, 7% O ₂	1.5-2	2
U. Arizona	70% < 74 μ m	1600 K*	1.2	2
*Flame temperature, self-sustained combustion.				

TABLE 7.3-41. - Fume formation - San Miguel (Texas) lignite

Facility	Coal Size	Gas Conditions	S.R.	Wt% < 0.5 μ m
PSIT	70% < 74 μ m	1500 K, 7% O ₂	1.5-2	0
PSIT	70% < 74 μ m	1500 K, 21% O ₂	4.5-6	1
MIT	63/75 μ m	1650 K, 20% O ₂	7-20	2

TABLE 7.3-42. - Fume formation - Loy Yang coals

Facility	Coal	Coal Size (μ m)	Gas Conditions	Wt% < 0.5 μ m
PSIT	LY 2301	70% < 74	1700 K, 7% O ₂	40
UA Run 39	LY 2301	70% < 74	1620 K	45
UA Runs 30/31	LY 2301	70% < 74	1500 K	16
MIT	LY 2301	63/75	1650 K, 20% O ₂	41
PSIT	LY 1953	70% < 74	1700 K, 7% O ₂	10
UA Run 50	LY 1953	70% < 74	1450 K	12
MIT	LY 1953	63/75	1650 K, 20% O ₂	33
MIT	LY 1953	63/75	1650 K, 50% O ₂	62
MIT	LY 1953	63/75	1650 K, 80% O ₂	84

TABLE 7.3-43. - Fume formation - Illinois #6 SOAP

Facility	Coal Size	Gas Conditions	Wt% < 0.5 μ m
PSIT	70% < 74 μ m	1700 K, 7% O ₂	7
UA Run 51	70% < 74 μ m	1570 K	1

TABLE 7.3-44. - Fume formation - Gravimelt 7A

Facility	Coal Size	Gas Conditions	Wt% < 0.5 μ m
PSIT	100% < 90 μ m	1700 K, 7% O ₂	15
UA Run 52	As received	1680 K	4
MIT	63/75	1650 K, 20% O ₂	61
MIT	63/75	1650 K, 50% O ₂	68
MIT	63/75	1650 K, 80% O ₂	73

TABLE 7.3-45. - Fume formation - Gravimelt 9C

Facility	Coal Size	Gas Conditions	Wt% < 0.5 μ m
PSIT	As received	1700 K, 21% O ₂	10
PSIT	100% < 90	1700 K, 7% O ₂	8
MIT	63/75	1650 K, 20% O ₂	33
MIT	63/75	1650 K, 50% O ₂	62
MIT	63/75	1650 K, 80% O ₂	84

TABLE 7.3-46. - Fume formation - Blend of EB/KY 9

Facility	Coal Size	Gas Conditions	Wt% < 0.5 μ m
MIT	63/75	1650 K, 20% O ₂	10
MIT	63/75	1650 K, 50% O ₂	27
MIT	63/75	1650 K, 80% O ₂	41
MIT	EB 63/75	1650 K, 20% O ₂	14
MIT	Ky #9 63/75	1650 K, 20% O ₂	7

both UA and PSIT. The higher levels observed at PSIT relative to UA are attributed to the difference in temperature, again demonstrating the sensitivity of fume formation to local gas conditions (contrast this with the general insensitivity of the size and composition distributions of the $> 1 \mu\text{m}$ ash particles to gas conditions).

In Tables 7.3-44 and 7.3-45, results obtained during combustion of the Gravimelt coals are presented. The fume levels were significantly higher under all circumstances compared to baseline bituminous coals (Tables 7.3-36 through 7.3-38). Sensitivity to combustion oxygen level (and hence particle combustion temperature) was again demonstrated by the MIT experiments.

Finally, in Table 7.3-46, MIT results for the blend and blend parent coals are summarized. Levels were comparable to those observed during experiments with the Phase I versions of these coals, as seen in Tables 7.3-36 and 7.3-39. The amount of fume generated during combustion of the blend was close to the calculated average of the Eagle Butte and Kentucky #9 fuels (weighted by the blending ratio).

In summary, two points can be made.

- the amount of fume produced during combustion of coals is sensitive to the particle combustion temperature, which varies with oxygen level and bulk gas temperature.
- a higher percentage of the ash was present in the submicron size range for the beneficiated coals as compared to the parent or raw coals examined in Phase I. This increase in fume level was attributed to the removal of minerals, which act as a sink for volatile species. The removal of minerals without the associated removal of organically associated inorganics would also increase the fraction in the submicron range, although not the absolute amount, by decreasing the amount of fly ash formed (i.e., decreasing the denominator in the ratio (submicron ash)/(total ash)).

A detailed discussion of ash vaporization and submicron fume formation is presented in Subsection 5.3.2 of this report.

7.4 Effect of Combustion Stoichiometry on Ash Formation: Reducing Conditions

Much of the work conducted under this program was conducted under oxygen rich conditions, ranging from a stoichiometric ratio of 1.2 in UA and some PSIT experiments to essentially infinite excess oxygen levels in dilute MIT experiments. This permitted the effect of oxygen concentration on ash formation to be examined in detail under conditions relevant to current coal-fired power generation systems. Future systems, including low-NO_x burners and advanced power generation technologies, will, however, conduct a portion of the combustion process at reduced oxygen concentrations or under reducing conditions. Limited experimentation was therefore carried out under this program to determine whether

stoichiometric combustion or combustion under slightly reducing conditions produced major changes in the size and composition distribution of the combustion-generated ash.

Combustion experiments were therefore carried out with Phase II samples of Eagle Butte and Kentucky No. 9 coals at PSIT to assess the effects of combustion conditions on ash chemistry. The stoichiometric ratio was varied by changing the feed rate of coal while maintaining a constant inlet gas composition of 7% oxygen in nitrogen. The gas temperature was held at 1700 K by setting the furnace wall temperature to 1773 K (1500°C). This resulted in experiments conducted at stoichiometric ratios of 0.9, 1.0, and 3.4 for Eagle Butte sub-bituminous coal, and 0.9, 1.0 and 2.6 for Kentucky #9 bituminous coal.

In Figure 7.4-1, volumetric ash particle size distributions determined from inverted CCSEM data obtained at UNDEERC are presented for the Eagle Butte coal as a function of combustion stoichiometry. The ash shows a slightly coarser particle size distribution under reducing conditions, but overall differences are small. The ash particle composition analysis for this coal is reported in Table 7.4-1. The formation of calcium and sodium aluminosilicates is slightly lower under reducing conditions than under either stoichiometric combustion or oxidizing conditions. Overall, however, differences in the distribution of ash particle compositions were slight among the three conditions examined. This is also reflected in the CCSEM surface compositional analysis reported in Table 7.4-2. Iron oxide concentrations decrease slightly as oxygen levels are increased, perhaps suggesting more complete dissolution of iron in the aluminosilicate ash particles (less iron on the particle surfaces). Additional analysis utilizing cross-sectioned samples would be required to confirm this.

Ash particle size distributions obtained from analysis of the Kentucky #9 ash produced at three different conditions are reported in Figure 7.4-2. Inverted surface measurements (i.e., samples were not cross-sectioned) were used for this analysis. Similar size distributions were noted for the reducing and oxidizing conditions, suggesting little effect of oxygen partial pressure on the ash particle size distribution for this range of conditions. For the intermediate case of stoichiometric combustion, a coarser size distribution was recorded. Although the reasons for this are unclear, it is possible that a few large iron oxide particles have biased the analysis. This is consistent with the data presented in Tables 7.4-3 and 7.4-4, where high iron oxide levels are reported in the stoichiometric combustion sample. In all other aspects, the data were similar at all three conditions.

Given the results of this preliminary study, we can conclude that iron and calcium aluminosilicate formation increases slightly as combustion oxygen level is increased; otherwise, the effect of changes in combustion stoichiometry have little effect on the size and composition distributions of the ash *for the range of conditions considered*. It is conceivable that under more severe reducing conditions such as those encountered with low-NO_x burners, there would be quantifiable effects. These "more extreme" reducing conditions were considered beyond the scope of this work, and hence were not explored.

FIGURE 7.4-1. CCSEM ash particle size distributions generated by combustion of Phase II Eagle Butte coal at three different stoichiometric ratios.

TABLE 7.4-1. - CCSEM ash composition as a function of O₂ concentration
Eagle Butte (wt% of ash)

Composition Class	S.R.*=0.9	S.R.=1.0	S.R.=3.4
Silica	5.5	4.9	7.1
Iron oxide	0.8	1.4	0.1
Calcium Oxide	0.0	0.2	0.6
Dolomite	4.7	5.1	7.3
Al-silicate	0.3	0.8	2.8
Ca Al-silicate	11.6	10.2	13.2
Na Al-silicate	6.6	9.9	8.0
Ca silicate	2.3	0.9	2.7
Ca aluminate	9.7	6.3	11.4
Ca-rich	0.9	1.7	2.8
Unknown	54.7	57.5	40.2
*S.R. = stoichiometric ratio			

TABLE 7.4-2. - Comparison of ash oxide compositions as a function of combustion oxygen level Eagle Butte (wt% as oxides)

Oxide	S.R.=0.9	S.R.=1.0	S.R.=3.4
Na ₂ O	0.7	0.9	0.7
MgO	5.4	6.6	4.4
Al ₂ O ₃	19.3	17.8	17.6
SiO ₂	26.5	21.2	30.6
K ₂ O	0.6	0.4	0.5
CaO	35.9	40.3	35.7
Fe ₂ O ₃	5.7	6.9	4.2
TiO ₂	2.5	2.6	3.4

Data from corrected CCSEM analysis of dispersed (surface) ash samples.

FIGURE 7.4-2. - CCSEM ash particle size distributions generated by combustion of Phase II Kentucky #9 coal at three different stoichiometric ratios

**TABLE 7.4-3. - CCSEM ash composition as a function of O₂ concentration -
Kentucky #9 (wt% of ash)**

Composition Class	S.R. = 0.9	S.R. = 1.0	S.R. = 2.6
Silica	15.4	12.6	14.4
Iron oxide	2.4	8.5	2.3
Calcite	1.4	1.9	1.8
Al-silicate	18.1	19.5	19.3
K Al-silicate	18.4	15.4	14.8
Fe Al-silicate	8.1	6.2	9.0
Ca Al-silicate	2.8	3.3	1.9
Na Al-silicate	0.0	0.1	0.2
Mixed Al-silicate	2.5	2.0	2.9
Fe silicate	1.4	0.5	0.3
Ca silicate	0.2	0.2	0.1
Si-rich	4.7	4.5	5.3
Ca-rich	0.9	0.8	1.0
Unknown	12.9	9.0	13.9
*S.R. = Stoichiometric ratio			

**TABLE 7.4-4. - Comparison of ash oxide compositions as a function of combustion
oxygen level - Kentucky #9 (wt% as oxides)**

Oxide	S.R. = 0.9	S.R. = 1.0	S.R. = 2.6
Na ₂ O	0.5	0.4	0.4
MgO	0.3	0.7	0.2
Al ₂ O ₃	18.4	16.9	19.0
SiO ₂	56.2	47.4	59.1
K ₂ O	2.8	2.3	2.6
CaO	5.1	7.4	5.0
Fe ₂ O ₃	12.2	21.2	9.8
TiO ₂	1.2	1.4	1.6
Data from corrected CCSEM analysis of dispersed (surface) ash samples.			

7.5 In-situ Measurements of Ash Particle Size Distributions

Prior to conducting pilot-scale combustion testing at SECV, PSIT conducted a joint testing program with the University of Arizona at the UA self-sustained reactor to assess operation of an Insitac PCSV-P in-situ measuring device. The PCSV-P is a near-forward scattering, single particle counting device housed in a water cooled probe, thus permitting insertion into hostile environments. Because of the single particle counting technique, it is not necessary to assume a shape for the particle size distribution (as is required by ensemble scattering devices). True individual particle counting in the 0.3 to 100 μm size range can therefore be obtained (Holve et al., 1986).

In this test program, experiments were conducted with four coals previously examined at PSIT and UA - Illinois #6, Beulah lignite, Loy Yang 2301, and Loy Yang 1953 - to permit comparison of the PCSV-P data with that measured by other sizing techniques. As discussed in Subsections 6.5.4.1 through 6.5.4.4 of this report, general agreement between the PCSV-P and cascade impactor measurements was obtained for all four coals, although the cascade impactor consistently reported a finer ash particle size distribution. This was attributed to the inability of the PCSV-P to detect particles smaller than approximately 0.5 to 1 μm , and the inclusion of unburnt carbon particles in the PCSV-P measurements.

A summary of this test series follows. Comparison with cascade impactor measurements is not included in this section, as it was discussed in detail in Sections 6.5.4.1 through 6.5.4.4 of this report.

7.5.1 Overview of Test Program

The objectives of the joint PSIT/UA test program were as follows:

- 1) Examine the effects of combustion scale and combustion temperature on ash particle size distributions (PSD's) in the University of Arizona's (UA) 3.0 kilogram per hour reactor.
- 2) Obtain in-situ measurements of ash particle size distributions with the Insitac particle counter sizer velocimeter probe (PCSV-P).
- 3) Obtain extractive samples with UA's isokinetic sampling probe for both cascade impactor measurements and CCSEM measurements and compare these results to the PCSV-P data.
- 4) Obtain extractive ash samples for Computer Controlled Scanning Electron Microscopy (CCSEM) and Atomic Absorption (AA).

Illinois #6, Beulah Lignite, and Loy Yang 2301 from Phase I of this program as well as Loy Yang 1953 from Phase II of this program were examined. Measurements and samples taken included PCSV-P particle size, concentration, and velocity measurements, cascade impactor

measurements, furnace temperature profiles, samples for CCSEM analysis, and continuous monitoring of CO, CO₂, total NO_x, and O₂ concentrations. PSIT was responsible for the PCSV-P measurements while UA was responsible for the operation of the reactor and all extractive samples. CCSEM analysis was performed by the University of Kentucky, while AA was performed at the University of Arizona.

A sketch of the UA reactor appears in Figure 7.5-1 along with labels showing where the sampling and the measurements took place. A detailed description of this reactor, including the standard method of operation, was presented in Subsection 6.1 of this report.

FIGURE 7.5-1. - Schematic diagram of UA combustor, showing PCSV-P sampling locations.

Testing was scheduled so that coal was burned every other day. On the days between the coal runs, the reactor was run on gas to "clean off" any residual ash. A brief discussion of the results follows on a coal by coal basis.

7.5.2 Test Results

Illinois # 6 (Parent)

Testing of the Illinois #6, UA burn 47, coal was conducted at a nominal feed rate of 1.3 kg/hr corresponding to a peak flame temperature of 1573 K. Measurements made with the PCSV-P appear in Figure 7.5-2. Each curve in the figure represents a separate run, plotted as a cumulative mass distribution. For particles greater than 10 microns there was a large discrepancy from run to run. This was attributed to the high carbon content of the ash, shown by analysis to be approximately 27%. This high level was attributed in part to the presence of the 10.2 cm PCSV-P cooling jacket in the relatively small 15.3 cm I.D. reactor, which decreased temperature downstream of the probe (see discussion, Subsection 6.5.4).

Despite the cooling effects of the PCSV-P, cascade impactor size distributions (measured without the PCSV-P) were in reasonable agreement with PCSV-P data. Perhaps

FIGURE 7.5-2. - Illinois #6 cumulative mass distributions measured with the PCSV-P at UA.

more importantly, the chemical composition of the ash, as measured by CCSEM, was consistent with that noted in previous experiments with the Illinois #6 coal at PSIT and UA. This is shown for several ternary systems in Figures 7.5-3 through 7.5-5. Fe-Al-Si compositions are plotted in Figure 7.5-3, K-Al-Si compositions in Figure 7.5-4, and Ca-Al-Si compositions in Figure 7.5-5. In each case, the distribution of compositions observed in these tests at UA at a flame temperature of 1573 K was comparable to those observed in prior testing of Illinois #6 at PSIT at a combustion temperature of 1650 K.

Beulah Lignite

Experiments were conducted at two different feed rates, corresponding to two different load conditions, in combustion testing of the Beulah lignite coal. The low load PCSV-P measurements appear in Figure 7.5-6. The conditions for this experiment were a peak flame temperature of 1430 K, achieved at a feed rate of 1.6 kg/hr. Good agreement from run to run was achieved, with most of the variability taking place in the larger sized particles. The high load PCSV-P measurements appear in Figure 7.5-7. In these runs, the peak flame temperature was 1520 K and the feed rate was 2.8 kg/hr. Again, there was good agreement with only minor differences occurring with the measurement of particles greater than 20 microns. The carbon content of the ash was 6.5%, considerably lower than that of the Illinois #6, and resulting in decreased run-to-run variability.

Loy Yang 2301 and 1953 Coals

The Loy Yang 2301 coal, studied in detail during Phase I of this program, was also examined at two feed rates. The PCSV-P measurements for the low feed rate experiment appear in Figure 7.5-8. The conditions for this run were a peak flame temperature of 1550 K achieved at a feed rate of 1.8 kg/hr. The stoichiometric ratio for this test was 1.2, consistent with all other experiments conducted at UA. For the Loy Yang 2301, good agreement among runs was noted. In particular, the large particle measurements were very close to each other. Figure 7.5-9 shows the results of measurements obtained under high load conditions, i.e., a peak flame temperature of 1693 K at a feed rate of 2.7 kg/hr. These measurements were also internally consistent. The carbon content of the ash trap sample was 9%, so there was a moderate amount of unburned carbon. The ash trap sample was a combination of both loads.

Loy Yang 1953 is similar to Loy Yang 2301, with a notable exception being the amount of sodium in the coal relative to the aluminosilicate content. This ratio was lower for the Loy Yang 1953, and therefore a reduced amount of submicron fume was anticipated as discussed previously (Subsections 3.3.3 and 7.3.2, plus extensive discussion in Section 6). The ash content of the Loy Yang 1953 was also higher than the ash content of the Loy Yang 2301 (2.9% versus 1.4%, dry basis). For these two reasons, a larger ash particle size distribution was expected during the combustion of Loy Yang 1953, assuming that unburned carbon levels were comparable.

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FIGURE 7.5-3. - Fe-Al-Si CCSEM ternary diagram for UA and PSIT Illinois #6.
 Each point represents at least one particle with the sum (Fe+Al+Si) greater than 80 mole%
 on an oxygen-free basis. Particles $1\ \mu\text{m} \leq dp \leq 10\ \mu\text{m}$. (a) UA; (b) PSIT.

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FIGURE 7.5-4. - K-Al-Si CCSEM ternary diagram for UA and PSIT Illinois #6. Each point represents at least one particle with the sum (K+Al+Si) greater than 80 mole% on an oxygen-free basis. (a) UA, $dp > 8 \mu\text{m}$; (b) PSIT, all particles.

FIGURE 7.3-5. - Ca-Al-Si CCSEM ternary diagram for UA and PSIT Illinois #6. Each point represents at least one particle with the sum $(\text{Ca} + \text{Al} + \text{Si})$ greater than 80 mole% on an oxygen-free basis. (a) UA, $dp > 8 \mu\text{m}$; (b) UA, $dp < 2 \mu\text{m}$ (c) PSIT, all particles.

FIGURE 7.5-6. - Beulah lignite cumulative mass distribution (low load) measured with the PCSV-P at UA.

FIGURE 7.5-7. - Beulah lignite cumulative mass distributions (high load) measured with the PCSV-P at UA.

FIGURE 7.5-8. - Loy Yang 2301 low load cumulative mass distributions measured with the PCSV-P at UA.

FIGURE 7.5-9. - Loy Yang 2301 high load cumulative mass distributions measured with the PCSV-P at UA.

Measurements were therefore conducted in the UA furnace with Loy Yang 1953 at a single feed rate. The peak flame temperature for these tests was 1430 K and the feed rate was 2.5 kg/hr. The PCSV-P measurements appear in Figure 7.5-10. The agreement was very reasonable with three of the six runs almost a direct overlay of one another. The carbon content of the ash was 17%. This is high but it may be a result of the high moisture delaying ignition in the reactor. (Because of time constraints, the coal was air dried for 1 day only, rather than the typical three.) Although unburned carbon was certainly a factor, it is apparent that the ash particle size distribution measured for the Loy Yang 1953 was greater than that measured for the Loy Yang 2301.

In conclusion, PCSV-P measurements were consistent from run-to-run for the Loy Yang and Beulah coals. This indicates that results from different experiments can be directly compared - i.e., the large UA facility operates in a consistent fashion from run-to-run. While some discrepancy was noted for the Illinois #6, it was attributed to the large percentage of unburned carbon for this sample. It is believed that the PCSV-P was contributing to elevated unburned carbon levels by quenching the combustion gases as a result of its large diameter relative to the combustion chamber. Thus, a facility of this size is perhaps the lower limit for use of the water-cooled probe. In all cases, however, measurements were qualitatively consistent with trends noted in cascade impactor sampling, as discussed in Subsection 6.5.4.

FIGURE 7.5-10. - Loy Yang 1953 cumulative mass distributions measured with the PCSV-P at UA.

7.5.3 Results as a Function of Combustion Temperature

A comparison of particle size distributions for Beulah Lignite at two different temperatures (loads) appears in Figures 7.5-11 and 7.5-12. The increase in particle number in the 2 to 10 μm size range at higher temperature shown in the differential plot of Figure 7.5-11 leads to the differences in cumulative mass distribution observed in Figure 7.5-12. This trend is qualitatively consistent with that observed on PSIT samples by CCSEM - decreasing cumulative ash PSD with increasing combustion temperature (Boni et al., 1990, Phase 1 Final Report).

FIGURE 7.5-11. - Differential Beulah Lignite ash particle size distributions (number basis) measured in-situ with the PCSV-P at the University of Arizona

FIGURE 7.5-12. - Cumulative ash particle size distributions (mass basis) measured in-situ at with the PCSV-P at UA. Constant ash density assumed.

7.6 PSIT/SECV Pilot Scale Combustion Testing

Under the auspices of an IEA Implementing Agreement on Coal Combustion Sciences (Annex I), PSIT conducted a joint testing program with the Herman Research Laboratories of the State Electricity Commission of Victoria (SECV), Australia, at the SECV 35 kg/hr pilot-scale combustion test facility. Experiments were conducted with the Phase I Beulah lignite provided by this program, Phase II Loy Yang 1953 (provided by SECV), and Loy Yang 1953 treated with an $\text{Mg}(\text{OH})_2/\text{MgCO}_3$ mixture and water-soluble $\text{Al}_2(\text{SO}_4)_3$ to reduce sodium levels (washing), produce refractory phases, and minimize fouling. Measurements/samples included complete coal characterization, reactor temperature profiles, 30 min and 4 hr uncooled deposition tests, 4 hr cooled deposition tests (furnace zone), extractive ash sampling, fouling test bank sampling, cascade impactor measurements, particle size/velocity/concentration measurements using the Insitac PCSV-P (by PSIT), and ESP ash hopper samples (size and chemical composition).

7.6.1 Background

Collaboration between the SECV and PSIT in the area of ash formation and deposition during low-rank coal combustion has been on-going since the initial stages of Phase I of this program. Initially coals were exchanged, with SECV providing PSIT with a sample of high sodium, low silica Loy Yang 2301 for combustion testing, and PSIT in turn providing SECV with a sample of crushed Beulah lignite. SECV then examined sodium evolution from the Beulah lignite in their electrothermal atomizer/atomic absorption apparatus, while the University of Kentucky examined the forms of chlorine in the Loy Yang via XAFS spectroscopy. During a subsequent visit to PSIT, MIT, and CalTech by Dr. George Domazetis of SECV, results were exchanged. SECV also provided PSIT with a copy of their combustion furnace chemistry code SCCOFF during this visit. As a result of this interchange, a jointly authored manuscript was published in Progress in Energy and Combustion Science (Srinivasachar et al., 1990). Subsequent to this visit, PSIT conducted the first in-situ measurements of alkali molecular species in a coal combustion environment, by measuring gas-phase NaCl levels via laser-induced photodissociation and fluorescence (LIPF), including the SECV Loy Yang 2301 coal as part of the test matrix.

The extensive interaction between PSIT and SECV has stemmed from complementary activities in the area of low-rank coal combustion. The participants in this DOE program - PSIT, MIT, CalTech, University of Arizona, University of Kentucky, and Foster-Wheeler - possess considerable expertise in the areas of sodium evolution, sodium-ash and calcium-ash interactions, and the formation of sticky ash particles. SECV (as well as CSIRO and the University of Newcastle) possesses considerable expertise in understanding deposition of these species, and development of techniques to control deposition. In addition, the experimental facilities available to this program in the U.S. range from single particle reactors to 2 kg/hr furnaces, while the SECV facility is a pilot-scale 35 kg/hr reactor. Continued collaboration, as implemented via an IEA Annex I agreement, provided this program with access to larger scale facilities and a wealth of practical experience in successfully controlling deposition.

7.6.2 Objectives and Description of Facilities

The specific objectives of these tests were as follows:

1. Continue the examination of the effects of combustor parameters ("combustion scale") on ash formation processes, by examining the Beulah lignite coal from this program in the SECV 35 kg/hr facility (≈ 1 MM Btu/hr) shown in Figure 7.6-1 and described in Table 7.6-1. SECV provided the test facilities and crew as part of the IEA Annex I Agreement.
2. Obtain in-situ ash particle size distribution (PSD) measurements with the Insitac PCSV-P for comparison to PSD's obtained from measurement of extracted samples.
3. Examine effects of refractory coal additive - soluble Al - on deposition.
4. Examine deposit initiation for comparison with PSIT lab tests and study deposit buildup and growth (4 hr experiment).

FIGURE 7.6-1. - Schematic diagram of the SECV 35 kg/h furnace showing sampling locations.

TABLE 7.6-1. - Operating parameter ranges for the SECV 35 kg/hr furnace

Factor	Limits	Typical
a) Coal feed rate at 15% moisture	2 to 60 kg/hr	35 kg/hr
b) Excess air at 35 kg/hr coal	0 to 100%	2 to 100%
c) Water addition at flame	0 to 70 kg/hr	-
d) Steam addition to secondary air	0 to 35 kg/hr	-
e) Peak flame temperature	-	1150° to 1350°C
f) Coal particle size - medial	10 to 200 μ m	
g) Tunnel gas temperature	850° to 1300°C	
h) Tube bank metal temperature	350° to 850°C	
i) Velocity in tunnel	0.4 to 1.25 m/s	
j) Combustion chamber diameter	60 cm	
k) Test section diameter	22.5 cm	

As shown in Figure 7.6-1, samples were taken from the combustion chamber and horizontal duct; these were extracted with quenched, water cooled sampling probes. Deposit samples taken from the test banks (cooled surfaces) were removed by extracting the entire test bank at the conclusion of a test and scraping the deposit sample from the tube. Deposit samples were also collected from a deposition probe that contained ceramic (hot) and water cooled (cold) sections. After extracting the probe from the combustion chamber, deposits were removed by scraping the surface of the probe. Electrostatic precipitator samples were collected from the ESP hopper at the conclusion of an experiment.

All samples were analyzed for bulk chemical composition by atomic absorption spectroscopy (AA) and for chemical phase by x-ray diffraction. In addition, extractive particulate samples collected from the combustion chamber ring 7 and the horizontal duct, and a composite sample collected from the ESP were analyzed by computer controlled scanning electron microscopy (CCSEM) for individual ash particle size and chemical composition. Mössbauer analysis to determine the chemical forms of iron in the samples was conducted at the University of Kentucky.

As mentioned above, tests were conducted with natural gas (as a background check), Phase I Beulah lignite, Phase II Loy Yang 1953, and Loy Yang 1953 treated with an $Mg(OH)_2/MgCO_3$ mixture and water-soluble $Al_2(SO_4)_3$ to reduce sodium levels, produce refractory phases, and minimize fouling. A four-test sequence was carried out with these fuels, as follows: Test 1 was conducted with Loy Yang 1953. During the test, large pieces of iron oxide were noted in the coal sample barrel, so the test was terminated prior to

completion. Test 2 was then conducted with Beulah lignite, test 3 with the treated sample of Loy Yang 1953, and finally, test 4 was conducted as a repeat of test 1 utilizing different drums of untreated Loy Yang 1953. A description of each of these fuels is presented in the following subsection.

7.6.3 Coal Analysis

Samples of each of the coals were analyzed at SECV for coal and ash composition. The proximate and ultimate analyses of the Loy Yang 1953 are presented in Table 7.6-2. Both the test 1 and the test 4 samples were comparable to the sample to the Loy Yang 1953 tested at PSIT, UA, and MIT; the only noteworthy difference being the elevated ash content of the test 4 sample. The proximate and ultimate analyses for the treated Loy Yang 1953 (test 3 sample) are presented in Table 7.6-3. Ash levels were higher than for the "parent" Loy Yang 1953 as a result of the additive treatment process. Interesting to note is the increase in volatile matter content subsequent to additive treatment. Finally, the proximate and ultimate analyses for the Beulah lignite coal are presented in Table 7.6-4. Little difference between the SECV sample and the Phase I program sample was noted.

TABLE 7.6-2. - Analysis of LY 1953 coal

	PSIT LY 1953	SECV Test 4 LY 1953	SECV Test 1 LY 1953
Proximate (dry)			
Fixed Carbon	44.4	46.4	45.6
Volatile Matter	52.7	49.8	51.5
Ash	2.9	3.8	2.9
Ultimate (dry)			
C	64.2	64.2	64.9
H	4.6	4.5	4.6
N	0.9	0.6	0.6
S	0.4	0.4	0.3
O	27.0	26.5	26.7
Ash	2.9	3.8	2.9

Coal particle size distributions for the three coal samples, as analyzed via Malvern (in ethanol) at UNDEERC, are presented in Tables 7.6-5 through 7.6-7. As the tables indicate, the Loy Yang coal was slightly coarser than either the treated Loy Yang or the Beulah. All, however, were approximately "utility grind," with approximately 70% passing through a 200 mesh or 75 μm screen. The 70% point for each coal was as follows: Beulah, 70% < 86 μm ; Loy Yang, 70% < 105 μm ; treated Loy Yang, 70% < 75 μm .

TABLE 7.6-3. - Analysis of treated Loy Yang 1953

	As Received (%)	Moist Free (%)	Moist/Ash Free (%)
Proximate analysis			
Moisture	23.40	N/A	N/A
Volatile matter	42.97	56.13	58.83
Fixed carbon (ind)	30.10	39.27	41.16
Ash	3.52	4.60	N/A
Ultimate Analysis			
Hydrogen	5.67	4.00	4.19
Carbon	46.04	60.13	63.03
Nitrogen	0.40	0.52	0.54
Sulfur	0.41	0.54	0.56
Oxygen (ind)	43.95	30.19	31.65
Ash	3.52	4.60	N/A
Calc. calorific value (Btu/hr)	7676		
As received hydrogen not including hydrogen from moisture: 3.06%			
As received oxygen not including oxygen from moisture: 23.12%			

TABLE 7.6-4. - Analysis of Beulah coal

	Phase I Sample	SECV Sample
Proximate (dry)		
Fixed Carbon	44.3	45.5
Volatile Matter	41.9	40.6
Ash	13.8	13.9
Ultimate (dry)		
C	59.1	61.5
H	4.2	3.9
N	1.2	0.9
S	1.9	1.0
O	19.8	18.8
Ash	13.8	13.9

TABLE 7.6-5. - Malvern coal PSD - Beulah

Size Microns	Under	% in Band	Size Microns	Under	% in Band
564.0	100.0	0.0	53.1	53.1	3.6
487.0	100.0	0.0	45.8	49.5	3.7
420.0	100.0	0.0	39.5	45.8	4.4
362.0	100.0	0.0	34.1	41.5	4.5
312.0	100.0	0.0	29.4	37.0	3.7
270.0	100.0	0.3	25.4	33.3	3.1
233.0	99.6	1.5	21.9	30.2	2.8
201.0	98.2	3.0	18.9	27.4	3.0
173.0	95.1	4.9	16.3	24.3	3.3
149.0	90.2	5.9	14.1	21.0	3.5
129.0	84.3	6.0	12.1	17.5	2.5
111.0	78.3	4.8	10.5	15.0	1.8
95.9	73.5	5.0	9.0	13.2	1.5
82.7	68.6	5.8	7.8	11.7	2.2
71.4	62.8	5.4	6.7	9.5	2.8
61.6	57.3	4.3	5.8	6.7	
Focal length = 300 mm Beam length = 14.3 mm Obscuration = 0.3029 Volume conc. = 0.0165 % Log. diff. = 4.09 Model indp D(v,0.5) = 46.7 μm D(v,0.9) = 148.0 μm D(v,0.1) = 6.9 μm D(4,3) = 62.2 μm D(3,2) = 22.5 μm Span = 3:0					

TABLE 7.6-6. - Malvern coal PSD - Loy Yang 1953

Size Microns	Under	% in Band	Size Microns	Under	% in Band
564.0	100.0	0.0	53.1	45.1	4.1
487.0	100.0	0.0	45.8	40.9	4.2
420.0	99.9	0.0	39.5	36.7	4.6
362.0	99.9	0.0	34.1	32.1	4.4
312.0	99.9	0.0	29.4	27.7	3.6
270.0	99.9	1.2	25.4	24.1	3.0
233.0	98.7	3.8	21.9	21.1	2.6
201.0	94.8	5.5	18.9	18.6	2.5
173.0	89.4	5.9	16.3	16.0	2.5
149.0	83.4	5.6	14.1	13.6	2.3
129.0	77.8	5.7	12.1	11.2	1.6
111.0	72.0	5.5	10.5	9.7	1.2
95.9	66.5	5.7	9.0	8.5	1.2
82.7	60.8	5.9	7.8	7.3	1.3
71.4	55.0	5.4	5.7	6.0	1.9
61.6	49.6	4.5	5.8	4.1	
Focal length = 300 mm Beam length = 14.3 mm Obscuration = 0.3090 Volume conc. = 0.0224% Log. diff. = 4.84 Model indep D(v,0.5) = 62.2 μ m D(v,0.9) = 175.4 μ m D(v,0.1) = 10.8 μ m D(4,3) = 76.4 μ m D(3,2) = 30.5 μ m Span = 2.6					

TABLE 7.6-7. - Malvern coal PSD - treated LY 1953

Size Microns	Under	% in Band	Size Microns	Under	% in Band
564.0	100.0	0.0	53.1	57.7	5.0
487.0	100.0	0.0	45.8	52.6	5.0
420.0	100.0	0.0	39.5	47.6	5.1
362.0	99.9	0.0	34.1	42.5	4.8
312.0	99.9	0.0	29.4	37.7	4.2
270.0	99.9	0.7	25.4	33.5	3.8
233.0	99.2	2.3	21.9	29.7	3.3
201.0	96.9	3.3	18.9	26.4	3.0
173.0	93.5	3.7	16.3	23.3	2.8
149.0	89.9	3.6	14.1	20.5	2.8
129.0	86.2	4.0	12.1	17.7	2.4
111.0	82.3	4.2	10.5	15.3	2.3
95.9	78.1	4.7	9.0	13.0	2.2
82.7	73.4	5.2	7.8	10.7	2.6
71.4	68.1	5.3	6.7	8.2	2.7
61.6	62.8	5.1	5.8	5.5	
Focal length = 300 mm Beam length = 14.3 mm Obscuration = 0.3984 Volume conc. = 0.0237% Log. diff. = 4.31 Model indp D(v,0.5) = 42.3 μm D(v,0.9) = 149.5 μm D(v,0.1) = 7.4 μm D(4,3) = 58.8 μm D(3,2) = 22.8 μm Span = 3.4					

Because all coals for this test program were pulverized at SECV rather than at Foster Wheeler, and because of the time between shipment and combustion testing of the Beulah, analysis of the specific coal samples employed was deemed necessary. For these coals, all analyses were conducted at UNDEERC. A few points need to be emphasized before the mineralogy of these coals is discussed. First, the Loy Yang sample discussed previously in Subsection 3.3.3, Table 4.5, and Subsection 7.3.2 of this report is not the Loy Yang 1953 sample tested at SECV. Mineralogical analysis discussed previously pertains to samples tested at PSIT, UA, and MIT; mineralogical analysis discussed in this section pertains to the sample of Loy Yang 1953 tested at SECV *only*. Second, although the SECV Beulah sample was also analyzed at the University of Kentucky (Table 4.6 of this report), the UNDEERC analysis presented in this section was used. This was done for purposes of consistency, so that all coals were analyzed at the same CCSEM facility.

Mineral distributions for the three coals are presented in Table 7.6-8. (Complete distributions are given in Appendix L). Quartz was present in moderate amounts in both Loy Yang samples. Kaolinite and pyrite/oxidized pyrite were the dominant phases observed in the Beulah (similar results were obtained in U. Kentucky analysis of this particular sample; see Table 4.6). Pyrite levels were lower than those observed in the Phase I sample of Beulah lignite previously tested under this program. For the untreated Loy Yang, most of the minerals fell into the "unknowns" category and were dominated by chlorine-rich compositions as shown in Table 7.6-9. Upon treatment with the aluminum and magnesium additives, these chlorine rich regions disappeared, consistent with previous studies of this treatment process (Vuthaluru et al., 1991). SEM photographs of the high chlorine regions observed in this coal are presented in Figure 7.6-2. In this figure, bright areas represent chlorine rich regions. Note the absence of these regions in the micrographs of the treated Loy Yang sample. High iron oxide concentrations observed in the treated Loy Yang are attributed to contamination because of their large size ($> 46 \mu\text{m}$; see Appendix L).

TABLE 7.6-8. - CCSEM mineral distributions of coals tested at SECV

Phase (wt%)	Loy Yang (1953)	Treated Loy Yang (1953)	Beulah
Quartz	7.5	16.5	4.6
Kaolinite	0	0.7	41.0
Montmorillonite	0	0.1	2.2
Pyrite	0.1	0.9	10.0
Pyrrhotite/Oxidized	0	7.6	6.0
Iron Oxide	0.4	24.5	1.5
Gypsum	0	3.4	15.4
Unknown	87.1	30.8	9.2

TABLE 7.6-9. - CCSEM chemical composition of Loy Yang "unknown" mineral categories: elemental mole%

	Na	Mg	Al	Si	P	C	Cl	K	Ca	Fe	Ti
Loy Yang (1953)	1	1	2	5	1	0	86	1	1	2	1
Loy Yang (1953) - Treated	3	2	6	15	1	4	36	2	6	24	2

Most of the minerals were included within the carbon matrix of these coals, with the exception of the iron oxide in the treated Loy Yang sample. This is shown in Tables 7.6-10 through 7.6-12. Each column represents the percentage of mineral that is included or excluded within a specific size fraction. The last two columns represent the total percentage of any given mineral that is included or excluded. The *total* amount of excluded mineral matter can be obtained by $100 \cdot \Sigma(f_m)(f_x)$, where f_m is amount (fraction) of the mineral contained in the coal, and f_x is the fraction of that mineral that is excluded. For the Beulah, approximately 25% of the minerals were excluded. Approximately 50% of the pyrite and pyrite products were excluded from the coal particles; this result was consistent with that inferred from previous CCSEM analysis of the Phase I Beulah. In the Phase I study, the existence of a large fraction of $> 20 \mu\text{m}$ pyrite minerals was assumed to indicate excluded material. Approximately 50% of the treated Loy Yang minerals and 10% of the parent Loy Yang minerals were excluded.

Mineral size distributions for these coals are presented in Figure 7.6-3. As mentioned above, the treated Loy Yang distribution is biased by the presence of the large iron oxide particles assumed to result from contamination in the treatment process. A size distribution with these particles and large "oxidized pyrrhotite" particles subtracted out is also presented for comparison. Even when modified, the treated Loy Yang contained the coarsest mineral distribution of the three coals sampled. Untreated Loy Yang contained the smallest mineral size distribution.

Finally, the chemical analysis of the ash for each coal is presented in Table 7.6-13. The Beulah sample was comparable to the Beulah examined during Phase I of this program (Table 3.15), whereas the Loy Yang 1953 evaluated at SECV differed in ash chemistry from samples tested at PSIT, UA, and MIT. In particular, more silica and less magnesia were noted in the sample tested at SECV.

7.6.4 Results: Ash Particle Size and Composition

Operating parameter ranges for the three coals are presented in Table 7.6-14. Test 4 data are shown for the Loy Yang 1953 coal, as this experiment was considered more reliable than test 1. In general, the testing proceeded smoothly. Short term variations in coal feed rate from 25 to 50 kg/hr (absolute) were occasionally observed, with corresponding changes in furnace exit gas temperature (FEGT) and exit oxygen levels (generally 5 to 7.5%). These variations were generally short-term, and often coincided with a person walking on the metal grate surrounding the coal feed hopper. Typically, feed rates were maintained at 35 to 40 kg/hr, with an FEGT of 900° to 950°C .

(a) Parent

FIGURE 7.6-2. - SEM of parent and treated LY 1953. Bright areas represent Cl.

(b) Treated

FIGURE 7.6-2. - SEM of parent and treated LY 1953. Bright areas represent Cl (Continued).

TABLE 7.6-10. - Included/excluded mineral analysis of Beulah Lignite coal tested at SECV
(all results are expressed on an area percent basis)

	Total wt%	% IN < 10	% EX < 10	% IN > 10	% EX > 10	% IN Total	% EX Total
Quartz	4.6	67.9	12.1	54.7	45.3	69.6	30.4
Iron Oxide	1.5	60.5	39.5	8.5	91.5	11.1	88.9
Calcite	0.1	0.0	0.0	0.0	100.0	0.0	100.0
Kaolinite	41.0	92.9	7.1	66.1	33.9	88.5	11.5
Montmorillonite	2.2	96.2	3.8	94.9	5.1	95.9	4.1
K-Aluminosilicate	0.2	34.1	65.9	100.0	0.0	79.2	20.8
Fe-Aluminosilicate	1.6	94.0	6.0	100.0	0.0	94.7	5.3
Ca-Aluminosilicate	1.1	91.5	8.5	0.0	0.0	91.5	8.5
Aluminosilicate	0.5	100.0	0.0	88.2	11.8	97.3	2.7
Mixed Silicates	0.1	100.0	0.0	0.0	0.0	100.0	0.0
Pyrite	10.9	24.8	75.2	51.7	48.3	47.1	52.9
Pyrrhotite	3.1	84.0	16.0	15.6	84.4	54.8	45.2
Oxidized Pyrrhotite	2.9	73.8	26.2	89.4	10.6	85.7	14.3
Gypsum	15.4	64.5	35.5	37.7	62.3	44.2	55.8
Barite	3.2	76.8	23.2	96.6	3.4	86.3	13.7
Gypsum/Barite	0.4	93.6	6.4	100.0	0.0	93.8	6.2
Gypsum/ Aluminosilicate	0.9	98.7	1.3	47.0	53.0	97.1	2.9
Si-Rich	1.1	100.0	0.0	45.8	54.2	37.7	52.3
Unknown	9.2	83.0	17.0	76.2	23.8	81.7	18.3

TABLE 7.6-11. - Included/excluded mineral analysis of untreated LY test 4 coal tested at SECV (all results are expressed on an area percent basis)

	Total wt%	% IN < 10	% EX < 10	% IN > 10	% EX > 10	% IN Total	% EX Total
Quartz	7.5	79.0	21.0	14.8	85.2	34.4	65.6
Iron Oxide	0.4	0.0	100.0	0.0	100.0	0.0	100.0
K-Aluminosilicate	0.1	0.0	0.0	0.0	100.0	0.0	100.0
Fe-Aluminosilicate	0.1	0.0	0.0	100.0	0.0	100.0	0.0
Ca-Aluminosilicate	0.1	32.8	67.2	100.0	0.0	38.4	61.6
Fe-Silicate	0.2	0.0	0.0	0.0	100.0	0.0	100.0
Si-Rich	4.2	100.0	0.0	94.9	5.1	99.5	0.5
Unknown	87.3	99.5	0.5	79.3	20.7	96.1	3.9

TABLE 7.6-12. - Included/excluded mineral analysis of treated Loy Yang 1953 tested at SECV (all results are expressed on an area percent basis)

	Total wt%	% IN < 10	% EX < 10	% IN > 10	% EX > 10	% IN Total	% EX Total
Quartz	16.5	81.9	18.1	26.6	73.4	44.2	55.8
Iron Oxide	24.5	17.2	82.8	22.2	77.8	22.1	77.9
Rutile	0.4	100.0	0.0	0.0	100.0	60.9	39.1
Alumina	0.8	56.0	44.0	27.4	72.6	48.4	51.6
Calcite	0.1	90.0	10.0	0.0	0.0	90.0	10.0
Kaolinite	0.7	88.9	11.1	0.0	100.0	86.1	13.9
Montmorillonite	0.1	100.0	0.0	100.0	0.0	100.0	0.0
K-Aluminosilicate	0.4	76.3	23.7	0.0	0.0	76.3	23.7
Fe-Aluminosilicate	0.1	100.0	0.0	0.0	0.0	100.0	0.0
Ca-Aluminosilicate	6.8	45.8	54.2	100.0	0.0	46.5	53.5
Aluminosilicate	0.5	100.0	0.0	0.0	0.0	100.0	0.0
Mixed Silicates	0.2	100.0	0.0	0.0	100.0	82.7	17.3
Ca-Silicate	0.6	90.9	9.1	0.0	0.0	90.9	9.1
Ca-Aluminate	0.1	100.0	0.0	0.0	0.0	100.0	0.0
Pyrite	0.9	69.9	30.1	0.0	0.0	69.9	30.1
Oxidized Pyrrhotite	7.6	8.1	91.9	1.2	98.8	2.1	97.9
Gypsum	3.4	79.1	20.9	0.0	100.0	75.6	24.4
Barite	0.2	100.0	0.0	0.0	0.0	100.0	0.0
Gypsum/ Aluminosilicate	0.7	73.3	26.7	0.0	0.0	73.3	26.7
Si-Rich	3.1	18.7	81.3	15.4	84.6	18.6	81.4
Ca-Si-Rich	1.4	65.6	34.4	58.7	41.3	64.0	36.0
Unknown	30.8	75.5	24.5	14.9	85.1	51.9	48.1

7.6.4.1 Natural Gas

Because furnace walls are not cleaned between runs, there was some concern over residual particulate matter contributing to the observed ash particle size distribution measurements. Test burns using natural gas indicated that this was not a problem, as particle count rates detected by the PCSV-P were statistically insignificant.

7.6.4.2 Beulah lignite

Experiments were conducted with the Beulah lignite coal sample at the conditions listed in Table 7.6-15. During these test, some difficulties in operating the PCSV-P were encountered during Beulah lignite combustion as a result of obscuration of probe optics. Nevertheless, several measurements on the furnace centerline, ring 7 (furnace exit region - see Figure 7.6-1) were made. PCSV-P particle size distributions obtained during combustion of the Beulah at 36 to 41 kg/hr feed rate, corresponding to a furnace temperature of 1080° to

FIGURE 7.6-3. - CCSEM mineral size distribution for coals tested at SECV.

TABLE 7.6-13. - Ash chemical composition analysis, SECV tests
(wt% of ash)

	Beulah	Loy Yang 1953 (Test 4)	Treated LY 1953
SiO ₂	21.6	39.7	19.9
Al ₂ O ₃	13.1	8.3	26.4
TiO ₂	0.5	0.5	1.4
Fe ₂ O ₃	12.2	9.0	10.9
CaO	14.4	2.1	2.5
MgO	4.7	9.6	12.1
Na ₂ O	3.6	6.8	1.9
K ₂ O	0.1	0.3	0.2
SO ₃	29.7	23.8	24.7
Cl (ppm of coal, dry basis)	200	4200	1700

TABLE 7.6-14. - Furnace parameters for SECV coal tests

	Beulah	Loy Yang 1953	Loy Yang 1953, Treated
Furnace temperature (ring 3)	1080° to 1115°C	1090° to 1130°C	1075° to 1125°C
Flame temperature*	1300°C	1250°C	1160°C
Furnace exit temperature	900° to 950°C	905° to 950°C	855° to 900°C
Coal feed rate	36.5 to 41 kg/h	40 to 41 kg/h	36.1 to 39.3 kg/h
Furnace exit O ₂	7.1 to 8.8%	5.5 to 7.3%	5.6 to 9%
Test bank 3 temperature	550° to 600°C (est.)	500° to 550°C	500° to 550°C
*Suction pyrometer measurement			

TABLE 7.6-15. - Sampling location conditions - Beulah lignite

Location	Gas Temperature	Surface Temperature	Residence Time (s)
Comb. Chamber R7	1100°C	N.A.	0.9
Deposition - Hot	1000°C (est.)	1000°C (est.)	0.9
Deposit. - Cold	1000°C (est.)	560°C	0.9
Horizontal Duct	900 to 950°C	-	1.1
Test Bank 1	-	unknown	1.6
Test Bank 3	-	550 to 600°C	1.6
ESP Inlet	290°C	-	2.5 (est.)
ESP Outlet	190°C	-	2.5 (est.)

1115°C and furnace exit conditions of 900° to 950°C and 7 to 9% oxygen, are shown in Figure 7.6-4. The median ash particle diameter for these experiments was approximately 15 μm , with 50% of the mass falling between 10 and 25 μm . This distribution was slightly smaller than the corresponding experiment conducted with this coal at the University of Arizona, where a median diameter of 20 μm was observed. Differences in residual carbon levels in the ash may account for this discrepancy; this will be resolved pending analysis of the SECV ash samples. Recall that the University of Arizona (UA) results were also narrowly distributed, with 50% of the mass falling between approximately 15 and 25 μm (Subsection 7.5).

FIGURE 7.6-4. - Beulah lignite ash PSD measured with the PCSV-P, ring 7 combustion chamber centerline.

Examination of the chemical composition of the Beulah ash revealed composition ranges identical to those observed in smaller scale testing at PSIT and UA. As discussed in Section 4 of this report, aluminosilicates dominated the ash. The sodium aluminosilicate phase previously reported (Boni et al., 1990; Helble et al., 1990) was again observed in samples obtained at SECV, as shown in Figure 7.6-5. Clearly this composition was not present in the coal initially (Figure 7.6-5a), but was formed during combustion at similar conditions at all facilities. This suggests that over the range of reactor sizes considered, reactor scale - i.e., particle mixing, oxygen profile (constant vs. decreasing), particle density, etc. - does not affect the chemical composition of the ash particles when combustion temperatures are comparable.

Calcium-rich silicates and aluminosilicates, however, were the dominant compositions observed in the ash, as discussed in Section 4 and seen in Figure 7.6-6. Calcium enrichment was observed in all particle size classes as shown in parts (b) and (c) of the figure. Similar trends and results were observed in prior testing of Beulah at PSIT and UA.

Samples collected from each sampling point were also analyzed for bulk chemical composition by AA at SECV. The results of this analysis for four key components are presented in Table 7.6-16 on a wt% oxide basis. Sulfur and sodium concentrations in the ash increased with increasing residence time in the system (corresponding to decreasing gas temperature), while iron oxide concentrations decreased slightly and calcium oxide concentrations showed little change. Several inferences can be drawn from these results.

(a) Mineral

(b) PSIT

FIGURE 7.6-5. - Beulah lignite ash Na-Al-Si ternary plots by CCSEM showing all particles with $\text{Na} + \text{Al} + \text{Si} \geq 80$ atom% (oxygen-free basis).

(c) UA

(d) SECV

FIGURE 7.6-5. - Beulah lignite ash Na-Al-Si ternary plots by CCSEM showing all particles with $\text{Na} + \text{Al} + \text{Si} \geq 80$ atom% (oxygen-free basis) (Continued).

FIGURE 7.6-6. - Ca-Al-Si ternary for Beulah ash, ring 7 combustion chamber extractive sample. All particles such that $\text{Ca} + \text{Al} + \text{Si} \geq 80$ atom%. a) all particles; b) $0.5 \leq dp < 10 \mu\text{m}$; c) $10 \leq dp < 80 \mu\text{m}$.

TABLE 7.6-16. - Chemical analysis of selected species in bulk ash samples - Beulah lignite

Location	SO_3 (wt%)	CaO (wt%)	Na_2O (wt%)	Fe_2O_3 (wt%)
Comb. Chamber R7	7.3	19.3	7.4	13.3
Deposition - Hot	3.8	18.0	6.7	16.6
Deposit. - Cold	8.8	18.0	5.0	15.8
Horizontal Duct	9.1	19.0	9.3	12.5
Test Bank 1	16.9	21.8	6.0	11.9
Test Bank 3	12.7	20.4	6.8	12.1
ESP (composite)	13.9	15.7	11.2	11.5

The increasing sodium and sulfur concentrations are suggestive of sodium sulfate formation at the cooler temperatures associated with longer residence times. Sulfur levels increase more rapidly than sodium levels (assuming stoichiometric sodium sulfate), however, suggesting the formation of other sulfated species. It is therefore likely that calcium

contained within the ash particles is sulfating as the particles traverse the reactor and deposit on surfaces, an observation consistent with increasing sulfur and constant calcium levels in the ash. The association of the highest iron concentrations with the deposition probe samples suggests deposition of an iron-containing species at early residence time. Similar conclusions are drawn from XRD analysis of these samples. Phases observed in the bulk ash samples by XRD are shown in Table 7.6-17.

TABLE 7.6-17. - Crystalline phases observed in Beulah lignite testing - XRD analysis

Phase	Location (Read Down Each Column)			
	Deposition Probe Ceramic	Deposition Probe Cooled	Test Bank 3	Precipitator (Fly Ash)
$\text{Ca}_2\text{Al}_2\text{SiO}_7$	✓	✓	✓	✓
CaSO_4	-	✓	✓	✓
Fe_2O_3	✓	✓	✓	✓
NaAlSiO_4	✓	✓	-	-
Na_2SO_4	-	-	-	✓
NaAlO_2	-	✓	-	-
SiO_2	-	✓	✓	✓
Deposition Probe - denotes deposition probe at or near ring 7 of combustion chamber "-" - indicates phase not observed in sample				

Detailed CCSEM analysis of ash samples collected from the combustion chamber, horizontal duct, and ESP was also conducted. In CCSEM analysis, 1200 (University of Kentucky analysis) or 2000 to 3000 (UNDEERC analysis) individual mineral or ash particles are analyzed for size and chemical composition. From these measurements, an overall chemical composition can be generated for comparison with bulk chemical analysis. Previous experience has shown that good agreement between CCSEM and bulk chemical analysis is usually obtained for ash samples generated from U.S. bituminous coals (Boni et al., 1990). For low rank coals such as the Beulah lignite considered here, agreement is generally poorer.

The reason for this can be understood by considering the method of chemical identification of CCSEM analysis. Compositions are identified by energy dispersive x-ray analysis, using x-rays emitted from the region of a particle excited by an incident electron beam. The penetration depth of a CCSEM electron beam is of order $1\text{ }\mu\text{m}$ into a particle. Correspondingly, excited X-rays used to identify the elemental composition of the excited region are emitted from the outer $1\text{ }\mu\text{m}$ only. For ash particles larger than a few μm in diameter, therefore, only the outer layers of the particle will be analyzed. Differences between bulk ash composition and CCSEM determined composition are therefore indicative of enrichment of certain species on the surface of the ash particles.

Table 7.6-18 presents a comparison of CCSEM and AA bulk ash composition for these experiments on a sodium and magnesium free basis. The slight depletion in CCSEM analysis of silicon, aluminum, and iron, and the slight enrichment of calcium and sulfur are suggestive of surface enrichment in calcium sulfate (and possibly calcium oxide), consistent with the inferences drawn from the bulk ash composition trends discussed above. Calcium enrichment of ash particle surfaces has been observed in previous laboratory studies at PSIT and the University of Arizona with this coal (Boni et al., 1990).

TABLE 7.6-18. - Comparison of CCSEM and AA ash compositions Na and Mg free basis for Beulah lignite ash samples (wt% oxides)

	CC-R7		HD		ESP	
	AA	CCSEM	AA	CCSEM	AA	CCSEM
Si	30	26	30	27	26	21.
Al	18	13	19	14	17	13.
Fe	16	13	15	14	14	13.
Ca	23	31	23	27	20	24.
K	0.2	1	0.2	0	0.2	1.
S	9	15	11	17	17	25.
Ti	0.6	2	0.6	2	0.5	2.

CCSEM analysis of individual ash particles also provides information on the change in particle composition ranges with time. Figures 7.6-7 through 7.6-10 are ternary composition diagrams for the Beulah coal, ash from the combustion chamber, ash from the horizontal duct, and ash from the ESP hopper. The coal sample was analyzed at UNDEERC and the ash samples were analyzed at the University of Kentucky. For these Na-Al-Si diagrams, each point represents ash particles with the stated composition on a molar basis. The height of each peak represents the number of particles having the identified composition. Only those particles containing greater than 80 mole% (Na+Al+Si) are included. As Figure 7.6-7 shows, the sodium concentration of quartz and aluminosilicate minerals in the coal is very low. Samples collected from the combustion chamber, however, clearly contain sodium-rich particles (Figure 7.6-8). A similar observation is made for the horizontal duct ash particle sample (Figure 7.6-9). A sample collected from the ESP (Figure 7.6-10) is similar, with a noted decrease in pure aluminosilicate particles (those not containing sodium or other modifier ion such as Ca). Sodium-rich ash particles of identical composition have been observed previously in laboratory combustion studies of this coal (Boni et al., 1990; Helble et al., 1991b)

FIGURE 7.6-7. - CCSEM ternary Na-Al-Si diagram for the Beulah coal tested at SECV. Each point represents a particle with Na + Al + Si of > 80 mole% (oxygen-free basis). The height of each peak indicated the number of particles of a given composition.

FIGURE 7.6-8. - CCSEM ternary Na-Al-Si diagram for Beulah ash sampled in the combustion chamber, ring 7 at SECV. Each point represents a particle with Na + Al + Si of > 80 mole% (oxygen-free basis). The height of each peak indicated the number of particles of a given composition.

FIGURE 7.6-9. - CCSEM ternary Na-Al-Si diagram for Beulah ash sampled from the horizontal duct at SECV. Each point represents a particle with Na + Al + Si of > 80 mole% (oxygen-free basis). The height of each peak indicated the number of particles of a given composition.

FIGURE 7.6-10. - CCSEM ternary Na-Al-Si diagram for Beulah ash taken from the ESP hopper. Each point represents a particle with Na + Al + Si of > 80 mole% (oxygen-free basis). The height of each peak indicated the number of particles of a given composition.

Ash particle size distributions determined by CCSEM analysis for ash from the combustion chamber, horizontal duct, and ESP are shown in Figure 7.6-11. The volume fraction of the smallest ($< 5 \mu\text{m}$) ash particles increases slightly as residence time increases, perhaps due to the addition of small calcium and sodium sulfate ash particles at lower temperatures (longer times). The statistical uncertainty in these measurements is $\pm \sim 5$ to 7% (absolute) (Boni et al., 1990, Section 7); the differences between the ESP and horizontal duct (convection section inlet) are within these bounds. Combustion chamber samples were significantly larger than either of the downstream ash samples.

In Figures 7.6-12 and 7.6-13, the ash particle size distributions for the combustion chamber and ESP are replotted, this time excluding any ash particles containing ≥ 20 mole% sulfur. No significant difference is noted in either sample when the data are inverted and plotted on a cumulative volume percent basis. This suggests that sulfate ash particles are not the principal reason why a smaller ash size distribution was observed in the ESP sample, relative to the combustion chamber sample. Because the CCSEM does not consider carbon particles when analyzing ash particles, residual carbon is probably not the cause for the observed difference. (Loss-on-ignition measurements were the same for each sample [Helble et al., 1991b]) It is therefore concluded that increasing sulfur content (Table 7.6-19) is primarily indicative of the sulfation of existing calcium rich ash particle surfaces, and not the formation of a $1 \mu\text{m}$ sulfate particles. Note that the formation of a fine sulfate fume would

FIGURE 7.6-11. - A comparison of ash particle size distributions for combustion chamber, horizontal duct, and ESP ash measured by CCSEM.
Size distributions are on a volume percent basis (from inversion of CCSEM surface data).

FIGURE 7.6-12 - CCSEM ash particle size distributions for the Beulah combustion chamber ash sample, with and without high sulfur content ash particles.

FIGURE 7.6-13 - CCSEM ash particle size distributions for the Beulah ESP ash sample, with and without high sulfur content ash particles.

TABLE 7.6-19. - Sulfur content of ash particle samples (CCSEM)

Location	% of Particles With S > 20%	Wt% SO ₃ (CCSEM)
Comb. Chamber R7	21	14
Horizontal Duct	26	16
ESP	53	23

not be detected by these measurements, as the lower limit of CCSEM resolution is approximately 0.5 to 1 μm .

The existence of calcium-rich ash particle surfaces is clearly evident from examination of Ca-Al-Si ternary diagrams. Figures 7.6-14 through 7.6-17 show coal and ash ternary diagrams for this system. Each point on the plot represents a specific molar composition of a particle containing greater than 80 mole% of the sum (Ca+Al+Si) on an oxygen-free basis. The height of each peak corresponds to the number of particles in the sample with the specified composition. In Figure 7.6-14 it is apparent that few calcium silicate or aluminosilicate minerals exist in the parent Beulah coal. Calcium concentrations in the mineral kaolinite (halfway along the Al-Si axis) are typically less than 10%. Examination of the combustion chamber, horizontal duct, and ESP ash samples in Figures 7.6-15, 7.6-16, and 7.6-17, respectively, show a marked increase in calcium aluminosilicate formation. Calcium-rich silicate compositions are also evident along the Ca-Si axis in the ESP ash sample (Figure 7.6-17).

Although the results are highly qualitative, the interactions between sodium, calcium, and aluminosilicate ash particles as a function of residence time can be observed from an examination of the major classes of ash particles present in a sample. Table 7.6-20 shows the major sodium and calcium containing ash particle categories observed in the three ash samples analyzed by CCSEM. In the table, the ordering of elements indicates their relative concentration, i.e., Na Al Si indicates that sodium was present in highest concentration, followed by aluminum and then silicon. The volume percentage of particles with these three elements being dominant and in the specified order is shown in the following columns. For the sodium aluminosilicate system, sodium decreases from being the major element to being third as residence time increases. This may be evidence of increasing reaction between the sodium and aluminosilicates, removing sodium from the outer surface of the particles. Decreasing calcium concentrations and increasing sulfur concentrations, also shown in Table 7.6-20, may be indicative of calcium sulfation with increasing residence time. These trends are consistent with those postulated from examination of CCSEM, AA, and XRD data previously discussed.

FIGURE 7.6-14. - CCSEM ternary Ca-Al-Si diagram for the Beulah coal tested at SECV. CCSEM analysis by JND EERC.

FIGURE 7.6-15 - CCSEM ternary Ca-Al-Si diagram for Beulah ash sampled in the combustion chamber, ring 7 at SECV. CCSEM analysis by U. Kentucky.

FIGURE 7.6-16 - CCSEM ternary Ca-Al-Si diagram for Beulah ash sampled from the horizontal duct at 3ECV. CCSEM analysis by U. Kentucky.

FIGURE 7.6-17 - CCSEM ternary Ca-Al-Si diagram for Beulah ash taken from the ESP hopper. CCSEM analysis by U. Kentucky.

TABLE 7.6-20. - Major Na and Ca ash compositions identified by CCSEM (vol%)

Ash Category	Comb. Chamber	Horizontal Duct	ESP
Si Al Na	11.5	11.7	15.9
Si Na Al	7.5	9.7	9.1
Na Si Al	4.7	3.5	2.5
Ca Si Al	5.2	4.0	3.5
Si Al Ca	3.0	4.5	3.1
Ca S	5.0	4.6	2.5
Ca S Na	2.4	2.3	4.1
S Ca Na	2.5	3.2	4.6
S Na Ca	1.6	2.6	8.3

Iron transformations were also examined in these tests through the use of Mössbauer analysis. An extractive sample collected from the combustion chamber, and deposit samples collected from the cooled deposition probe and the test banks were analyzed for iron phases. As the results in Table 7.6-21 show, the formation of the fully oxidized hematite phase increased with increasing residence time. Iron glass concentrations were also higher in the deposit samples than in the extracted sample, suggesting that the long residence times associated with a deposit may be necessary for some of the iron glass to form.

Although the chemical composition of the ash particles collected in the SECV test does not vary significantly from the compositions identified in PSIT and University of Arizona (UA) tests, the size distribution of the ash particles does. In Figure 7.6-18, ash particle size distributions for PSIT and SECV tests are compared on an area basis (similarity between PSIT and UA samples has been discussed previously - Boni et al., 1990). Ash particle sizes measured in the SECV tests were considerably finer than those measured in PSIT laboratory testing. Examination of the mineral size distributions (Figure 7.6-19) reveals a much finer *mineral* size distribution for the Beulah coal studied at SECV, however. Analysis of the Beulah coal psd by Malvern techniques (ethanol as dispersant) revealed a coal psd similar to that of the coal used in the PSIT and UA laboratory test (Boni et al., 1990; Helble et.al., 1991a), thus eliminating coal grind as a reason for the observed difference (Figure 7.6-20). Speculation centers on degradation of the large pyrite minerals previously identified, as the SECV sample was in storage for over two years prior to testing.

In summary, analysis of Beulah lignite coal and ash samples by AA, CCSEM, and XRD techniques confirm prior laboratory scale identification of sodium aluminosilicate ash particles (of nepheline composition) forming during the combustion process. Their presence

**TABLE 7.6-21. - Mossbauer analysis of SECV Beulah ash samples
(% of total iron in phase)**

Sample	Hemotite	Magnetite	Ferric Glass
Combustion Chamber	21	50	24
Cooled Deposition Probe	30	36	34
Test Bank 1	69	-	31
Test Bank 2	69	-	31

in the SECV ESP samples confirms their formation was not due to the small scale or sampling conditions employed in the PSIT and UA laboratory studies. The presence of sodium aluminosilicates was observed at early times (combustion chamber samples) and at temperatures above the dewpoint of sodium species. This suggests that the aluminosilicate forms during combustion, either within the burning char particle or via a gas-solid reaction. Calcium rich surface compositions were also identified, again similar to PSIT and UA test results. Sulfation of these calcium rich surfaces was inferred from the results at longer residence times. In

FIGURE 7.6-18. - Comparison of PSIT/SECV and PSIT Beulah lignite ash particle size distributions on an area basis.

C-0883

FIGURE 7.6-19. - Beulah lignite mineral size distributions for PSIT and PSIT/SECV samples.

C-0884

FIGURE 7.6-20. - Beulah lignite coal particle size distributions (Malvern analysis except as noted).

contrast to the chemical composition results, ash particle size distributions measured at the SECV 1 million Btu/hr furnace were much finer than those identified at the UA or PSIT reactors, 10 to 100 times smaller in scale. A finer mineral distribution in the SECV Beulah coal sample is believed responsible.

7.6.4.3 Loy Yang 1953 Brown Coal

Experiments were conducted with the parent Loy Yang 1953 coal sample on two separate occasions, denoted test 1 and test 4. During test 1, large pieces of iron oxide were found in the bottom of the first coal barrel, and may have contaminated the coal. This test was therefore terminated, and subsequently repeated with a new sample of Loy Yang 1953 as test 4. Most of the results presented in this section are therefore taken from test 4; limited analysis of test 1 samples is also presented.

For tests conducted with Loy Yang 1953, sampling occurred at the conditions identified in Tables 7.6-22 and 7.6-23. No significant difference was observed in operating conditions between runs. PCSV-P measurements of ash particle size distribution for the untreated LY 1953, Test 4, at the ring 7 centerline are shown in Figure 7.6-21. For these runs, the coal feed rate was 30 kg/hr, corresponding to a furnace temperature of approximately 1100°C and an FEGT of 905° to 950°C. Three of the four runs shown were virtually identical, with a median particle diameter of 45 μm observed. The size distribution was broader than that observed for the Beulah, with the middle 50% of the mass residing

TABLE 7.6-22. - Sampling location conditions - Loy Yang 1953, Test 1

Location	Gas Temperature	Surface Temperature	Residence Time (s)
Comb. Chamber R7	1100°C	N.A.	0.9
Deposition - Hot	1000°C (est.)	1000°C (est.)	0.9
Deposit. - Cold	1000°C (est.)	600°C	0.9
Horizontal Duct	800 to 850°C	-	1.1
Test Bank 1	-	unknown	1.6
Test Bank 3	-	500 to 550°C	1.6
ESP Inlet	295°C	-	2.5 (est.)
ESP Outlet	210°C	-	2.5 (est.)

TABLE 7.6-23. - Sampling location conditions - Loy Yang 1953, Test 4

Location	Gas Temperature	Surface Temperature	Residence Time (s)
Combustion Chamber R7	1110°C	N.A.	0.9
Deposition - Hot	1000°C (est.)	1000°C (est.)	0.9
Deposition - Cold	1000°C (est.)	600°C	0.9
Horizontal Duct	800 to 850°C	-	1.1
Test Bank 1	-	unknown	1.6
Test Bank 3	-	500 to 550°C	1.6
ESP Inlet	312°C	-	2.5 (est.)
ESP Outlet	165°C	-	2.5 (est.)

FIGURE 7.6-21. - Loy Yang 1953 ash PSD measured with the PCSV-P, ring 7 combustion chamber centerline.

between 25 and 65 μm . Measurements obtained within 5 mm of the reactor wall (Figure 7.6-22) were also identical with these three, indicating uniform particle distribution throughout the combustor. The outlying run in Figure 7.6-21 demonstrated a 20% increase in the number of particles observed during the fixed measurement period, but was identical to the other runs in all other aspects.

The chemical composition of the ash particles extracted from the horizontal duct was significantly different from that of the Beulah lignite, as expected. In Figure 7.6-23, a sodium-aluminum-silicon ternary plot if all particles containing greater than 80 atom% Na+Al+Si demonstrates the absence of the nepheline-like phase observed in combustion of the Beulah. Sodium aluminosilicate formation is minimal for this coal, suggesting that all of the sodium initially present in the Loy Yang (13.5% of the ASTM ash) vaporizes during combustion and recondenses in the submicron size range, which is not characterized by CCSEM (0.5 to 1.0 μm cutoff). Calcium-aluminum-silicon is presented in Figure 7.6-24, and iron-aluminum-silicon in Figure 7.6-25. No evidence of aluminosilicate formation is seen in these diagrams. Magnesium aluminates and aluminosilicates with a broad range of chemical composition were observed, as shown in Figure 7.6-26. The broad composition range suggests that a specific phase was not formed. The formation of the magnesium-containing particles likely results from the interaction of the organically bound magnesium

FIGURE 7.6-22. - Loy Yang 1953 ash PSD measured 50 mm from the wall of the combustion chamber (ring 7) with the PCSV-P.

FIGURE 7.6-23. - Na-Al-Si ternary, Loy Yang 1953 extracted from the horizontal duct.
All particles such that $\text{Na} + \text{Al} + \text{Si} \geq 80$ atom %.

FIGURE 7.6-24. - Ca-Al-Si ternary, Loy Yang 1953. All particles such that $\text{Ca} + \text{Al} + \text{Si} \geq 80$ atom%.

FIGURE 7.6-25. - Fe-Al-Si ternary, Loy Yang 1953. All particles such that $\text{Fe} + \text{Al} + \text{Si} \geq 80 \text{ atom\%}$.

FIGURE 7.6-26. - Mg-Al-Si ternary, Loy Yang 1953 ash, horizontal duct.
All particles such that $Mg + Al + Si \geq 60$ atom%.

with fine included aluminosilicate minerals; a lack of magnesium silicate formation suggests a lack of included quartz. Small numbers of zinc-containing particles were also observed, as shown in Figure 7.6-27. These were introduced into the system (or the coal) subsequent to test 1, as indicated in the test 1 and 4 comparison of Figure 7.6-28. Because Zn was only detected in the additive-treated coal, and only in the ESP sample, it was assumed that it originated from residual run 3 ESP sample (see following section, discussion of treated coal).

Chemical analysis of ash and deposit samples collected from combustion of Loy Yang 1953 during test 4 is shown in Table 7.6-24. Major differences were noted in chemical composition among the samples. In the high temperature deposition probe samples, silicates - possibly containing iron - were the only significant depositing species. As temperature decreased, the fraction of silica in a given sample decreased because of increasing deposition of sodium and magnesium species, either through condensation or thermophoretic deposition. X-ray diffraction analysis of these samples, shown in Table 7.6-25, indicated the existence of crystalline iron oxide in the deposit samples. XRD cannot identify the presence of amorphous phases (e.g., iron glasses). Mössbauer analysis, however, indicated 37% of the iron was present in a glassy phase in deposit samples (Table 4-79). These results suggests that iron silicates either formed during combustion to create a sticky layer, or were formed in the deposit from the interaction of iron and other depositing silicates. At lower temperatures, magnesium and sodium species present in the submicron fume begin to comprise a significant fraction of any deposit. Note that alumina - containing species are absent from most deposit samples, suggesting that these phases are not sticky (contrast with calcium aluminosilicates formed during Beulah lignite combustion).

FIGURE 7.6-27. - Zn-Al-Si ternary, Loy Yang 1953 ash, horizontal duct.
All particles such that $\text{Zn} + \text{Al} + \text{Si} \geq 60$ atom%.

CCSEM was also used to determine the chemical composition of ash particles greater than approximately $1\ \mu\text{m}$ in diameter. These results are shown for horizontal duct (extractive sample) and ESP samples in Table 7.6-26. The significant increase in sodium, sulfur, and to a lesser extent magnesium concentrations in the ESP sample suggests that sulfated coatings are forming on the ash particles. Because the CCSEM only sees the outer $1\ \mu\text{m}$ of a particle, the composition remains undetected. Thus, for the ESP sample, silicates are present in the core of the particles, and sodium and magnesium sulfates are on the surfaces. At the time of collection of the horizontal duct sample, these coatings had not formed.

Ash particle size distributions determined by CCSEM analysis are presented in Figure 7.6-29 for Test 4 samples and Figure 7.6-30 for Test 1 samples. In both cases, the size distribution for ash collected from the ESP was finer than that for ash collected from the horizontal duct. The addition of sulfated particles to the sample downstream of the horizontal duct appears to have contributed in part to the reduction in size.

7.6.4.4 Loy Yang 1953 Brown Coal Treated with Al and Mg

Previous work has shown that addition of aluminum to Loy Yang brown coal reduces the amount of sodium-rich ash formed, and causes a decrease in deposition in a laboratory scale reactor (Vuthaluru et al., 1991). To assess the impact of additives on ash formation and deposition in a pilot scale combustor, a sample of the Loy Yang 1953 brown coal was treated with an $\text{Mg}(\text{OH})_2/\text{MgCO}_3$ mixture and water-soluble $\text{Al}_2(\text{SO}_4)_3$ prior to testing.

(a) Test 1

(b) Test 4

FIGURE 7.6-28. - Al-Zn-Mg ternary, Loy Yang 1953 ash, ESP.
All particles such that $\text{Al} + \text{Zn} + \text{Mg} \geq 80$ atom %.

TABLE 7.6-24. - Chemical analysis of Loy Yang 1953 Test 4 ash and deposit samples (wt%)

Element	Dep. Probe Ceramic (s)	Dep. Probe ceramic (L)	Dep. Probe (cooled)	Test Bank 1	Test Bank 3	Precip. (flyash)
SiO ₂	82.9	79.2	53.1	36.1	32.3	20.3
Al ₂ O ₃	1.8	2.3	4.8	9.2	10.1	15.4
Fe ₂ O ₃	9.0	9.1	10.3	9.5	9.2	8.2
CaO	0.6	1.0	1.5	3.0	3.2	4.2
MgO	1.5	2.3	4.4	11.2	12.9	12.8
Na ₂ O	2.2	3.4	12.2	13.6	14.8	9.6
K ₂ O	0.4	0.46	0.16	0.17	0.19	0.20
TiO ₂	0.2	0.2	0.3	0.6	0.6	0.6
SO ₃	<0.1	0.6	7.6	12.9	14.0	5.0
P ₂ O ₅	<0.1	<0.1	<0.1	<0.1	0.1	0.2
Chloride (as % Cl)	nd	<0.1	5.5	1.5	2.5	2.6
Loss on ignition (%)	0.1	0.6	1.6	1.0	0.8	11.6

(s) - denotes short term (approximately 30 min.)
(L) - denoted long term (approximately 4 h)

TABLE 7.6-25. - Crystalline phases observed in Loy Yang 1953 Test 4 - XRD analysis of ash and deposits

Phase	Location			
	Dep. Probe Ceramic (S)	Dep. Probe Ceramic (L)	Dep. Probe Cooled (S)	Precipitator (flyash)
Na ₂ SO ₄	-	-	✓	-
NaCl	-	-	✓	✓
Fe ₂ O ₃	✓	✓	✓	✓
SiO ₂	✓	✓	✓	✓
MgAl ₂ O ₄	-	-	-	✓
MgO	-	-	-	✓

S - denotes short-term (approximately 30 min)
L - denotes long-term (approximately 4 hr)
"Dep. Probe" - denotes deposition probe at or near ring 7 of combustion chamber
- - indicates phase not observed in sample

TABLE 7.6-26. - CCSEM chemical composition analysis of Loy Yang 1953 Test 4 samples (wt%)

	Horizontal Duct	ESP
SiO ₂	45	8
Al ₂ O ₃	14	27
Fe ₂ O ₃	13	9
CaO	10	8
MgO	11	16
Na ₂ O	3	12
SO ₃	2	17
Other	2	3

FIGURE 7.6-29. - CCSEM ash particle size distributions for ash collected during combustion of Loy Yang 1953 coal, test 4.

FIGURE 7.6-30. - CCSEM ash particle size distributions for ash collected during combustion of Loy Yang 1953 coal, test 1.

After drying to approximately 25% water by weight, the coal was burned at 30 kg/hr in the SECV reactor. The furnace operating conditions used in these experiments are presented in Table 7.6-27.

Particle size distributions measured with the PCSV-P during combustion of the treated Loy Yang 1953 are presented in Figure 7.6-31. The five runs shown were nearly identical with one another, indicating extremely stable combustor operation with this fuel. Measurements were again taken at the centerline of ring 7, near the furnace exit. A median diameter of 60 μm was observed for these experiments, perhaps due to the presence of residual carbon in the sample. Malvern analysis of an extracted ash sample (in 80% isopropanol/20% water) at SECV demonstrated a distinct peak near 500 μm , suggestive of large pieces of unburnt char.

CCSEM chemical analysis of a treated Loy Yang ash sample extracted from the horizontal duct of the furnace indicated fewer Na aluminosilicate particles, as seen in Figure 7.6-32. This is due in part to a reduction in coal sodium levels from 4000 ppm to 1600 ppm (SECV analysis); the addition of magnesium and aluminum to the coal may also have contributed. Some calcium aluminosilicate formation was observed, as evidenced by the increased height of the peaks in the center of the ternary Ca-Al-Si diagram in Figure 7.6-33. Note that these peaks have disappeared in the ESP sample shown in part (c) of the figure, indicating that the particles have been coated with other compounds (sulfates, possibly zinc compounds). Although the expected magnesium and aluminum - rich particles

TABLE 7.6-27. - Sampling location conditions - treated Loy Yang 1953, Test 3

Location	Gas Temperature	Surface Temperature	Residence Time (s)
Comb. Chamber R7	1100°C	N.A.	0.9
Deposition - Hot	1000°C (est.)	1000°C (est.)	0.9
Deposit. - Cold	1000°C (est.)	500°C	0.9
Horizontal Duct	800 to 850°C	-	1.1
Test Bank 1	-	unknown	1.6
Test Bank 3	-	500 to 550°C	1.6
ESP Inlet	318°C	-	2.5 (est.)
ESP Outlet	163°C	-	2.5 (est.)

FIGURE 7.6-31. - Loy Yang 1953 treated ash PSD measured at ring 7 combustion chamber (centerline) with the PCSV-P.

(a) Coal

(b) Horizontal Duct, Sample

(c) ESP Sample

FIGURE 7.6-32. - Na-Al-Si ternary, treated Loy Yang 1953 ash.
All particles such that $\text{Na} + \text{Al} + \text{Si} \geq 80$ atom%.

FIGURE 7.6-33. - Ca-Al-Si ternary, treated Loy Yang 1953 ash.
All particles such that $\text{Ca} + \text{Al} + \text{Si} \geq 80$ atom%.

were observed in the sample (Figure 7.6-34), the most striking difference from the untreated Loy Yang was the increase in zinc concentrations in the ash (Figure 7.6-35). Zinc and magnesium did not interact significantly, as shown in Figure 7.6-36. Extensive zinc aluminate and aluminosilicate formation indicates high zinc levels in the coal, originating either from the additive or the water used to prepare the treated coal.

Chemical analysis of ash and deposit samples collected during this experiment is presented in Table 7.6-28. Several trends in composition with increasing residence time/ decreasing gas temperature are apparent. First, the silica and iron oxide content of the samples decreases with time. Second, alumina and magnesia contents increase with increasing time. Calcium levels are approximately constant throughout the four samples. From these pieces of data, several conclusions can be reached. It is apparent that calcium silicates or calcium aluminosilicates are not contributing to deposit formation for this coal; if they were, an increase in calcium concentration in test bank samples would have been observed. Also as residence time increases, aluminum/magnesium compounds are forming and being collected with the ash. These do not appear in early deposit samples, likely because temperatures are too high for their deposition.

XRD analysis of samples collected from the cooled deposition probe (combustion chamber sampling), third test bank, and ESP are presented in Table 7.6-29. As expected

FIGURE 7.6-34. - Mg-Al-Si ternary, treated Loy Yang 1953 ash. Horizontal duct sample, all particles such that $Mg + Al + Si \geq 60$ atom%.

FIGURE 7.6-35. - Zn-Al-Si ternary, treated Loy Yang 1953 ash. Horizontal duct sample, all particles such that $\text{Zn} + \text{Al} + \text{Si} \geq 60$ atom%.

FIGURE 7.6-36. - Al-Mg-Zn ternary, treated Loy Yang 1953 ash. ESP sample, all particles such that $\text{Zn} + \text{Al} + \text{Mg} \geq 80$ atom%.

TABLE 7.6-28. - Chemical analysis of treated Loy Yang 1953 Test 3 ash and deposit samples (wt%)

Element	Dep. Probe (cooled)	Test Bank 1	Test Bank 3	Precip. (flyash)
SiO ₂	18.4	15.6	12.7	7.1
Al ₂ O ₃	16.9	18.1	21.1	27.6
Fe ₂ O ₃	12.3	11.4	9.3	5.4
CaO	3.1	3.0	2.3	1.9
MgO	9.4	10.6	12.5	15.5
Na ₂ O	7.3	8.2	7.9	4.0
SO ₃	11.1	13.2	12.1	3.6
ZnO	13.2	14.0	16.0	18.0
Chloride (as % Cl)	<0.1	<0.1	0.1	3.3
Loss on ignition (%)	4.0	1.8	1.2	10.6
(s) denotes short term (approximately 30 min) (L) denoted long term (approximately 4 h)				

TABLE 7.6-29. - Crystalline phases observed in Loy Yang 1953 (treated) testing - XRD analysis

Phase	Location		
	Dep. Probe Cooled (S)	Test Bank 3	Precipitator (flyash)
CaAl ₂ SiO ₇	-	-	✓
Na ₂ SO ₄	✓	✓	-
NaCl	-	-	✓
Fe ₂ O ₃	✓	✓	✓
FeAl ₂ O ₄	-	-	✓
(MgFe) ₂ SiO ₄	✓	-	✓
MgFe ₂ O ₄	-	-	✓
MgAl ₂ O ₄	✓	-	-
SiO ₂	✓	✓	-
ZnO	✓	✓	✓
Other Zn	-	✓	-
S	-	denotes short-term (approximately 30 min)	
L	-	denotes long-term (approximately 4 hr)	
"Dep. Probe"	-	denotes deposition probe at or near ring 7 of combustion chamber	
-	-	indicates phase not observed in sample	

from the above discussion, no evidence of calcium aluminosilicates was found in deposit samples. It is possible that the initial sticky phase collected on the probe surface was magnesium iron silicates, as these were identified by XRD. Mössbauer analysis of the iron phases revealed the presence of a significant glassy iron compound (51% of the iron; Table 4-79); this may have contributed to initial deposit formation.

CCSEM was used to analyze the outer approximately 1 μm surface of ash samples collected from the horizontal duct and ESP. As shown in Tables 7.6-30 and 7.6-31, particle surfaces were zinc and aluminum rich in both cases. The increase in sodium, magnesium, and sulfur concentrations with increasing residence time, reflected in the ESP data of Table 7.6-31, is indicative of the formation of sulfates on the surface of the ash particles. Decreasing silica concentrations with time suggests that silica is in the core of the ash particles, and hence obscured from the CCSEM once the surface coatings have formed. Complete CCSEM analysis of these samples is available elsewhere in this report (Tables 4-72 and 4-73).

Ash particle size distributions presented in Table 7.6-30 (area) and Figure 7.6-37 (volume) demonstrate a decrease in particle size with increasing residence time. Recall that the same trend was observed in the parent Loy Yang 1953 experiments (tests 1 and 4). Although sulfation is occurring as the particles move downstream, this does not appear to be the reason for the increase in the amount of ash in the 10 to 20 μm size range in the ESP sample. It is possible that samples collected from the extractive probe were agglomerated slightly, as they were collected at higher temperature. Further analysis would be needed to confirm this.

7.6.5 Comparison of Coals - Ash Particle Size Distributions

A comparison of PCSV-P measured particle size distributions for a typical experiment for each coal are plotted in Figure 7.6-38. The second line plotted for the LY 1953 represents a measurement taken at the combustor wall. Beulah lignite produced the smallest ash particles, while particles of 60 μm median diameter were obtained from combustion of the treated Loy Yang. Residual carbon in the sample is expected to be the major cause of this difference. The general trend, however, was consistent with CCSEM-measured ash particle size distributions obtained on samples collected from the horizontal duct (Figure 7.6-39), which are blind to the presence of residual carbon. The difference between treated and untreated Loy Yang coals was, however, much smaller for the CCSEM-measured ash. Similar trends were observed in ESP samples for the three coals (Figure 7.6-40). Median diameters were smaller in all cases for the CCSEM as compared to the PCSV-P.

Cascade impactor measurements (Brink Instrument) were used to determine the fraction of the ash present in the submicron size range, as the PCSV-P and the CCSEM are ineffective below 0.5 to 1 μm in diameter. The treated Loy Yang produced the largest fraction of submicron ash (Table 7.6-32), while the Beulah at 3.3 wt% in the submicron range produced the smallest. For the Beulah lignite previously studied at PSIT and UA, 2% of the ash was present in the submicron range; for the Loy Yang 1953 at PSIT, 10 to 15% was in the submicron range (Subsection 7.3.6).

TABLE 7.6-30. - CCSEM analysis of treated LY 1953 samples (Test 3)

(a) Horizontal Duct

Species	Surface Area	Area Distribution						
		0.0-2.5	2.5-5.0	5.0-10	10-20	20-40	40-80	80-500
Al Mg Zn	10.1	13.0	35.0	39.0	13.0	0.0	0.0	0.0
Al Zn Mg	12.6	27.0	28.0	36.0	9.0	0.0	0.0	0.0
Al Zn S	4.6	22.0	32.0	38.0	9.0	0.0	0.0	0.0
Al Zn Si	5.9	30.0	36.0	28.0	6.0	0.0	0.0	0.0
Al Zn Fe	5.1	27.0	25.0	39.0	9.0	0.0	0.0	0.0
Others	13.6	32.0	22.0	28.0	19.0	0.0	0.0	0.0
Others	48.0	18.0	18.0	28.0	24.0	9.0	3.0	0.0
Totals	100.0	22.0	23.0	31.0	18.0	4.0	2.0	0.0

(b) ESP

Species	Surface Area	Area Distribution						
		0.0-2.5	2.5-5.0	5.0-10	10-20	20-40	40-80	80-500
Al Mg Zn	20.2	11.0	12.0	28.0	45.0	5.0	0.0	0.0
Al Zn Mg	17.3	10.0	26.0	32.0	30.0	2.0	0.0	0.0
Zn Al Mg	8.3	31.0	28.0	26.0	15.0	0.0	0.0	0.0
Al Zn Cl	4.3	6.0	42.0	18.0	32.0	2.0	0.0	0.0
Zn Al Cl	5.7	20.0	40.0	30.0	11.0	0.0	0.0	0.0
Others	4.4	45.0	55.0	0.0	0.0	0.0	0.0	0.0
Others	39.8	18.0	29.0	29.0	22.0	2.0	0.0	0.0
Totals	100.0	17.0	27.0	27.0	26.0	2.0	0.0	0.0

TABLE 7.6-31. - CCSEM chemical composition analysis of treated LY 1953 samples (Test 3) (wt%)

	Horizontal Duct	ESP
SiO ₂	6	1
Al ₂ O ₃	33	31
Fe ₂ O ₃	10	4
CaO	4	3
MgO	5	12
Na ₂ O	7	12
SO ₃	3	9
ZnO	28	25
Other	4	3

FIGURE 7.6-37. - CCSEM ash particle size distributions for ash collected during combustion of treated Loy Yang 1953 coal, test 3.

FIGURE 7.6-38. - Comparison of ash particle size distributions obtained from combustion of three coals and measured with the PCSV-P at SECV.

FIGURE 7.6-39. - Comparison of CCSEM ash particle size distributions obtained from combustion of three coals; sample from horizontal duct.

FIGURE 7.6-40. - Comparison of CCSEM ash particle size distributions obtained from combustion of three coals; sample from ESP.

TABLE 7.6-32. - Cascade impactor data for ash samples obtained in SECV tests

	Beulah Lignite	LY 1953	LY 1953, Treated
Stages 0-6	96.7	81.6	65.8
Final filter	3.3	18.4	34.2

7.6.6 Deposition Results

Deposit samples were collected using a deposition probe, inserted into the combustion chamber. The deposition probe consisted of an air cooled stainless steel tube, coupled to an uncooled ceramic tip attached via a water-cooled holder. The metal surface of the deposition probe was cooled to approximately 600°C, while the ceramic tube was in thermal equilibrium with the surrounding gases. During an experiment, the probe was held in the combustion chamber for approximately 30 min and then withdrawn. The ceramic tip was then removed, a new one installed, and the probe re-inserted into the furnace for a period of 4 to 5 hours. At the conclusion of an experiment, deposit samples were removed from the

cooled portion of the probe by brushing them into sample containers. Ceramic tips were removed with the deposit intact and stored for subsequent SEM analysis.

Deposits were also collected on cooled test banks located downstream in the horizontal duct, and designed to simulate leading edge convective surfaces. Two test banks, each cooled by compressed air flow, were used in these tests. The leading or first bank consisted of a single row of stainless steel tubes, 27 mm outer diameter by 175 mm long. The second bank, located in the third opening (moving downstream) and hence designated Test Bank 3, consisted of three rows of similar tubes. Thermocouples embedded in the walls of one tube from each bank were used to monitor metal surface temperature (typically 500° to 600°C). At the end of an experiment, the banks were removed and allowed to cool before the deposit was brushed off.

In examining the samples collected on the deposition test banks, deposits of 1.5 to 2 in. thickness were noted for the Beulah lignite, as shown in Figure 7.6-41 (lead test bank, #1). These were significantly larger than those observed for either the Loy Yang 1953 (Figure 7.6-42) or the treated Loy Yang (Figure 7.6-43). Although the higher ash content of the Beulah certainly contributes, the thickness of the deposits is also indicative of a stickier ash at the conditions of the tests (see Table 7.6-14).

FIGURE 7.6-41. - Test bank deposits, Beulah Lignite (test 2).

FIGURE 7.6-42. - Combustion chamber (top) and test bank (bottom) deposits, Loy Yang 1953 (test 4).

FIGURE 7.6.43. - Combustion chamber (top) and test bank (bottom) deposits, treated Loy Yang 1953 (test 3).

Phase analysis (XRD) of the deposits collected from the test banks for the three coals is shown in Tables 7.6-33 and 7.6-34. Calcium sulfate, calcium aluminosilicate, and iron oxide were all observed in the Beulah test bank deposit (test bank #3). As the deposit was scraped from the test bank prior to analysis, it was impossible to determine whether there was enrichment of certain phases nearer the tube surface. Using the ceramic deposition probe as an indicator of the state of the particles prior to impacting the cooled test banks, the presence of sodium aluminosilicates and calcium aluminosilicates suggests these may have been the species initiating the impaction-driven deposition (Table 7.6-35 - uncooled and Table 7.6-36 - cooled). High calcium and low sulfur levels in the 30-min uncooled deposition probe sample were also consistent with this hypothesis. For the Loy Yang samples, and particularly for the treated Loy Yang coal, only small amounts of deposit were collected on the ceramic deposition probe. Iron oxide and silica were the principal crystalline phases observed, although a silicate was found in the treated Loy Yang deposit. Because there was no pyrite in the Loy Yang coals, it is unlikely that molten iron phases contributed to the deposition. Instead, it is speculated that iron-silica glass mixtures, which are invisible to the XRD, initiated deposition for these coals at high temperature. The observed iron oxide and silica phases may have been associated with these glassy particles, as incomplete dissolution of iron in silicates has been repeatedly observed in this program (Subsection 6.8).

TABLE 7.6-33. - Crystalline phases observed in deposition test bank 1 samples - XRD analysis

Phase	Coal		
	Beulah lignite	Loy Yang 1953 (Test 4)	Treated Loy Yang 1953
$\text{Ca}_2\text{Al}_2\text{SiO}_7$	-	-	-
CaSO_4	✓	-	✓
Fe_2O_3	✓	✓	✓
Na_2SO_4	-	✓	✓
NaAlO_2	-	✓	-
NaCl	-	✓	-
SiO_2	✓	✓	✓
ZnO	-	-	✓
Zn phases	-	-	✓
"- " - indicates phase not observed in sample			

TABLE 7.6-34. - Crystalline phases observed in deposition test bank 3 samples - XRD analysis

Phase	Coal		
	Beulah lignite	Loy Yang 1953 (Test 4)	Treated Loy Yang 1953
$\text{Ca}_2\text{Al}_2\text{SiO}_7$	✓	-	-
CaSO_4	✓	-	-
Fe_2O_3	✓	✓	✓
Na_2SO_4	-	✓	✓
NaCl	-	✓	-
SiO_2	✓	✓	✓
ZnO	-	-	✓
Zn phases	-	-	✓
"- " - indicates phase not observed in sample			

TABLE 7.6-35. - Crystalline phases observed in ceramic deposition probe samples - XRD analysis

Phase	Coal		
	Beulah lignite	Loy Yang 1953 (Test 4)	Treated Loy Yang 1953
$\text{Ca}_2\text{Al}_2\text{SiO}_7$	✓	-	-
NaAlSiO_4	✓	-	-
Fe_2O_3	✓	✓	✓
$(\text{MgFe})_2\text{SiO}_4$	-	-	✓
SiO_2	-	✓	✓
Zn phases	-	-	-
"- " - indicates phase not observed in sample			

TABLE 7.6-36. - Crystalline phases observed in cooled deposition probe samples - XRD analysis

Phase	Coal		
	Beulah lignite	Loy Yang 1953 (Test 4)	Treated Loy Yang 1953
$\text{Ca}_2\text{Al}_2\text{SiO}_7$	✓	-	-
CaSO_4	✓	-	-
NaAlSiO_4	✓	-	-
NaAlO_2	✓	-	-
Na_2SO_4	-	✓	✓
NaCl	-	✓	-
Fe_2O_3	✓	✓	✓
$(\text{MgFe})_2\text{SiO}_4$	-	-	✓
MgAl_2O_4	-	-	✓
SiO_2	✓	✓	✓
Zn phases	-	-	-
"-" - indicates phase not observed in sample			

Chemical analysis of the Beulah lignite test bank deposits (Table 7.6-37) indicates similarity to ash particles collected before (extractive) and after (precipitator) the cooled tubes, suggesting that over the course of the run (4+ hr), all ash species eventually deposited. For the untreated Loy Yang, iron oxides and silica represented the only major species observed in uncooled deposits (Table 7.6-24). Because of the high sodium content of the coal, sodium chloride and sodium sulfate were observed in cooled deposition probe samples. As seen in Table 7.6-24, sticky particles at high temperatures (uncooled deposition probe samples) were predominantly iron and silica-rich, while deposits collected on the tests bank surfaces contained sodium, chlorine, and sulfur, consistent with XRD analysis of the deposits.

Deposit samples collected during combustion of the treated Loy Yang coal were light, of low density, and easily removed from tube and test bank surfaces, suggesting the presence of refractory phases. For this coal, zinc oxide and other zinc phases dominated the ash (Table 7.6-34), owing to the elevated zinc levels discussed previously. Zinc-rich compositions were not observed in uncooled (Table 7.6-35) or cooled (Table 7.6-36) deposition probe samples, suggesting that these phases were not depositing by inertial

TABLE 7.6-37. - Chemical analysis of Beulah (Test 2) ash and deposit samples (wt%)

Element	Dep. Probe Ceramic (s)	Dep. Probe cooled	Horizon. Duct	Test Bank 1	Test Bank 3	Precip. (flyash)
SiO ₂	28.8	26.8	24.6	23.7	24.1	20.8
Al ₂ O ₃	16.0	15.4	15.2	13.3	13.9	13.5
Fe ₂ O ₃	16.6	15.8	12.5	11.9	12.1	11.5
CaO	18.0	18.0	19.0	21.8	20.4	15.7
MgO	5.9	5.9	5.6	6.1	5.7	5.2
Na ₂ O	6.7	5.0	9.3	6.0	6.8	11.2
K ₂ O	0.6	0.1	0.15	0.09	0.1	0.18
TiO ₂	0.6	0.5	0.5	0.6	0.5	0.4
SO ₃	3.8	8.8	9.1	16.9	12.7	13.9
Loss on ignition	0.9	0.1	1.3	0.7	0.2	2.7
(s) denotes shot term (approximately 30 min) (L) denoted long term (approximately 4 h)						

impaction. Their existence in extractive samples collected in the horizontal duct suggests that the zinc phases were either forming by condensation in the collection probe at this location, or were not sufficiently sticky to adhere to the deposition probe surfaces. Magnesium-rich phases were also observed in the deposition probe samples, although they did not appear in the test bank 3 deposits.

For the Beulah lignite, the normalized chemical composition for several key elements from these samples, as determined at SECV and taken from the data in Table 7.6-37, is plotted in Figure 7.6-44. SO₃ concentrations were highest in the longest residence time (coolest temperature) deposits, indicating substantial sulfation of calcium within the ash. Iron oxide concentrations were slightly higher at shorter residence times, possibly suggesting deposition of large molten pyrite-derived products. Calcium oxide concentrations were highest in samples collected from the cooled deposition tube banks, possibly indicating the existence of sticky calcium aluminosilicate ash particles at this point in the system. Differences in calcium oxide and iron oxide concentrations along the length of the test facility were relatively small.

Deposit and extractive particle sample compositions for ash samples generated during combustion of Loy Yang 1953 brown coal, and Loy Yang 1953 treated with soluble

FIGURE 7.6-44. - Normalized deposit compositions as a function of position for Beulah lignite testing.

aluminum and magnesium additives are shown in Figure 7.6-45. The sodium, chlorine, and silicon contents of the deposits and the ash all decreased upon addition of the refractory additives. As noted in prior quarterly reports, the deposits generated during combustion of the treated Loy Yang were "fluffy" and hence easily removed. This suggests that this treatment process may be a viable means of controlling deposition during combustion of Loy Yang coals.

For the untreated Loy Yang and the Beulah lignite coals examined in testing at SECV, ceramic deposit samples were also sectioned and analyzed by SEM and energy-dispersive x-ray analysis at the University of Kentucky. Treated Loy Yang 1953 samples were not analyzed because of a lack of significant deposit formation for this coal. For the untreated Loy Yang 1953, test 1 deposits were iron-rich, likely due to the iron contamination of the coal sample. Test 4 deposits demonstrated considerably lower amounts of iron in the deposit. Iron oxide and silicon were observed as distinct regions, with some melting at the interface between compounds. It is not clear whether this interface formed on the deposit surface, or was formed during combustion and contributed to deposition. For the Beulah lignite, an initial iron-rich layer was accompanied by calcium and sodium aluminosilicate regions. Little mixing between calcium and sodium-rich particles was observed, suggesting that these particles deposited as sodium or calcium aluminosilicates.

These results are presented in detail in Subsection 4.5.6 of this report.

FIGURE 7.6-45. - Deposit and particle samples for ash generated during combustion of Loy Yang 1953 and treated Loy Yang 1953 at SECV. "Cyclone" refers to samples removed with an extractive sampling probe slightly downstream of the combustion chamber exit. "Precip" refers to samples removed from the electrostatic precipitator hopper.

7.6.7 Summary

During Phase II of this program, PSI Technology Co. conducted a joint experimental program with the State Electricity Commission of Victoria (SECV). Three separate areas were considered: 1) examination of combustion scale effects on the chemistry of individual ash particles; 2) examination of deposit compositions as a function of position (i.e., temperature) within the SECV 35 kg/h reactor; and 3) examination of the effects of adding soluble aluminum and magnesium compounds to the Loy Yang 1953 coal prior to combustion as a means of controlling ash deposition.

One of the objectives of the tests conducted at SECV was to examine the effects of combustion scale on the chemistry of individual ash particles. Previous work conducted at PSIT and the University of Arizona had demonstrated that the distributions of individual particle compositions obtained in the PSIT 1,000 to 10,000 Btu/h reactor were the same as those obtained in the University of Arizona 100,000 Btu/h facility. These similarities suggested that the fundamental processes controlling ash particle formation were dominated by the coal particle size, coal mineralogy, and overall combustion conditions (temperature, oxygen) and not combustor scale (i.e., heating rate and particle number density in the flow stream). To pursue this work further, additional tests were conducted at the SECV 35 kg/h (nominal 1 million Btu/h) facility with Beulah lignite coal from this program. Analysis of the Beulah sample at SECV revealed it to be similar to those tested previously in this program, although CCSEM mineralogical analysis indicated that the SECV sample had a smaller mineral size distribution. As a result, ash particle size distributions were smaller at SECV, but more importantly, the *distribution of chemical compositions observed previously for this coal was again identified at SECV*. This indicates that the size of the combustor does not affect the processes governing the distribution of chemical compositions in the ash. For the range of scales considered, small scale tests can therefore be used to assess the ash chemical composition distributions without the need to conduct pilot scale tests.

Deposition testing also indicated that the "sticky particle" mechanism for deposit initiation by inertial impaction held true at the pilot facility. In Beulah lignite laboratory-scale combustion tests at PSIT, the formation of sticky calcium aluminosilicates was postulated to be the cause for deposit initiation. These same particles were observed in high temperature deposit samples collected at SECV. At lower temperatures more appropriate to convective pass conditions, the formation of condensed or fine-particle phases such as sodium and calcium sulfates was found to be more important in initiating deposits. This was true for all of the coals considered. Addition of a soluble aluminum/magnesium compound to the Loy Yang coal was seen to be an effective way to reduce the formation of the latter type of deposit.

7.7 Fundamental Ash Particle Stickiness Study

During Phase I of this program, experiments to measure the stickiness of collections of ash particles as a function of their chemical composition were conducted. Utilizing soda-lime-silica glass as a synthetic ash compound, it was determined that a critical viscosity range existed for deposition by inertial impaction. That is, for viscosities above critical, ash particles would not adhere to tube surfaces, while for viscosities below critical, sticking would occur. In these experiments, for the range of particle kinetic energies expected upon inertial impact with cooled surfaces in a utility boiler, the range of approximately 10^5 to 10^7 Pa·s (kinetic-energy dependent) was sufficient to cause adhesion. Note that this viscosity range is several orders-of-magnitude higher than the flow viscosities sometimes used to characterize a coal's ash deposition tendency.

Deposition tests subsequently conducted with the Phase I coals demonstrated a wide range of ash particle stickiness behavior. The experimental procedure and results of these tests were described in detail previously (Boni et al., 1990). Briefly, ash particles are accelerated toward an uncooled tube surface using the probe shown in Figure 7.2-3. A fraction of this accelerated flow impacts the surface of a tube in cross flow; a fraction of the impacting particles subsequently sticks to the surface. Collection efficiency, η_c , is therefore defined as $\eta_c = \eta_I \eta_s$, where η_I = the fraction of particles impacting the surface and η_s equals the fraction of impacting particles that stick. η_I is based upon Stokes parameter calculations and is only determined for those particles traversing the flow cross section of the impaction tube. In other words, the relevant ash mass flow is determined from (total ash flow) $(A_{\text{projected tube}})/(A_{\text{cross section, flow}})$. Uncooled surfaces were used to permit an assessment of *particle* properties relevant to sticking. At constant temperature and similar impaction velocities, the stickiness of the coal ashes was found to be San Miguel > Beulah, Eagle Butte > Kentucky #11 > Kentucky #9, Upper Freeport, Illinois #6 > Loy Yang 2301. In this ranking, reproduced in Figure 7.7-1, particle size was subsumed - i.e., the results do not account for different impaction efficiencies that may result from differences in ash particle size. Note, however, that this is not a significant correction except for the low ash Loy Yang coal. What this ranking does represent is the relative tendency of these coals to initiate deposition at identical conditions. For these coals, it was determined that calcium-rich aluminosilicates were the primary contributors to high stickiness values. Results from this study were summarized in Subsection 8.3.7 of the Phase I Final Report.

7.7.1 Extraneous Mineral Study

The coal results briefly described above indicate that reduced aluminosilicate particle viscosities, resulting from interaction with calcium and other modifier ions during combustion, were a probable cause for this behavior. This suggested that a detailed study of deposit initiation should focus on the role of aluminosilicates during and subsequent to coal combustion.

As the coal experiments have demonstrated, aluminosilicate behavior can vary significantly from coal-to-coal because of differences in mineralogy and organically bound

FIGURE 7.7-1. - Comparison of collection efficiencies for Phase I coals at 1500 K combustion gas temperature.

species concentrations (detailed summary in Phase I Final Report). This can be seen in the ternary diagrams of Figures 7.7-2 through 7.7-4. In these figures, each composition represents an individual particle containing at least 80% of the sum (Ca+Al+Si), while the height of each bar represents the number (corrected and normalized) of particles of the particular composition. As indicated in Figure 7.7-2, combustion of an Illinois #6 bituminous coal at 1650 K, 7% oxygen showed only limited interaction between kaolinite (represented by the cluster of points with approximately 40 to 50% Al along the Al-Si axis) or illite (20 to 40% Al, Al-Si axis) and dispersed calcium species. For low-rank coals, however, much more extensive interaction was observed between kaolinite and dispersed calcium. This is evident from comparison of Figure 7.7-3, a Beulah lignite mineral ternary diagram showing kaolinite clustering at the Al-Si axis, with Figure 7.7-4, combustion-derived ash compositions for the same coal.

To study the stickiness of aluminosilicate-derived ash particles in more detail, kaolinite, montmorillonite, and nepheline transformations under combustion conditions were recently examined. Experiments were conducted under simulated combustion gas conditions of 0 to 3% oxygen in nitrogen at temperatures up to 1500°C. Morphological examination of these particles was conducted by scanning electron microscopy (SEM) on an Amray Model 1820 SEM. Chemical analysis of individual particle and deposit samples was by energy-dispersive x-ray analysis (EDAX).

FIGURE 7.7-2. - Illinois #6 ash Ca-Al-Si ternary diagram. 1650 K, 7% O₂.
Each composition represents at least one ash particle containing
 ≥ 80 mole% Ca+Al+Si.

FIGURE 7.7-3. - Beulah Ca-Al-Si ternary mineral diagram.

FIGURE 7.7-4. - Beulah ash Ca-Al-Si ternary diagram: 1500 K, 7% O₂.

Kaolinite was chosen as being representative of mineral matter in bituminous coals which may not add modifier ions during combustion, while montmorillonite and nepheline are more typical of reaction-formed ash products. Montmorillonite and kaolinite were obtained from the Source Clays Depository at the University of Missouri, Rolla, while the nepheline sample was obtained from the National Museum of Natural History, catalogue number 82524. The chemical composition for three of these samples is given below in Table 7.7-1. For the nepheline sample, CCSEM analysis at the University of Kentucky indicated that the sample consisted of a major nepheline phase (1/1/1 molar amounts sodium/aluminum/silicon) containing 6-10% potassium as an impurity. In addition, the sample contained potassium aluminosilicates (Figure 7.7-5) with 0 to 8% sodium as an impurity. CCSEM analysis of this sample is described further in Subsection 4.4 of this report.

TABLE 7.7-1. - Mineral sample chemical composition

	Kaolin*	Kaolin**	Montmorillonite
SiO ₂	51.6	51.2	67.7
Al ₂ O ₃	46.4	44.9	19.7
TiO ₂	1.6	2.4	0.3
Fe ₂ O ₃	0.2	1.1	1.6
FeO	0.1	0.2	0.1
MgO	0	0	7.2
CaO	-	-	3.2
Na ₂ O	0	0	0.1
K ₂ O	0.1	0.1	0.2
*Well-crystallized sample			
**Poorly crystallized sample

FIGURE 7.7-5. - K-Al-Si ternary diagram for nepheline sample.

7.7.1.1 Kaolinite

Experiments were first conducted with kaolinite to determine whether any observable morphological changes occurred under combustion gas conditions of 1725 K, 0 to 3% oxygen, 2.9s residence time. In Figure 7.7-6, an SEM micrograph of the untreated well-crystallized kaolinite shows typical large crystals surrounded by a high concentration of submicron-sized particulate. The chemical composition of five randomly sampled large particles ranged from 42 to 44% alumina with a balance of silica, consistent with the bulk chemical analysis of Van Olphen and Fripiat (1979) reported in Table 7.7-1. The morphology and chemical composition of the poorly-crystallized kaolinite sample (K-PC) were identical to the well-crystallized sample (K-WC), although an occasional particle with ca. 5% (weight) potassium (as oxide) was observed in the K-PC sample.

As expected, little change was observed in either sample subsequent to reaction in 3% oxygen at 1725 K for 2.9s. This is shown for the K-WC sample in Figure 7.7-7.

7.7.1.2 Montmorillonite

The montmorillonite clay sample was obtained from the Source Clays Depository at the University of Missouri - Columbia. Samples were mined from several well-characterized locations, steam dried, pulverized in a hammer mill, remixed, and then riffled prior to shipping. No additives were used in the preparation of these clays. The montmorillonite was mined in Apache County, Arizona. Detailed analyses of the sample has been collected and published (Van Olphen and Fripiat, 1979); the chemical composition of the montmorillonite sample according to this reference is 60.4 wt% silica, 17.6% alumina, 0.2% titania, 6.5% magnesia, 2.8% calcium oxide, and 0.3% total alkali oxide. Iron oxide levels were reported as 1.42% ferric oxide, and 0.08% ferrous oxide. Additional terms (to sum to 100%) represent weight loss upon heating.

K-WC (raw)
42 to 44% Al_2O_3
no impurities

V-491a

FIGURE 7.7-6. - SEM micrograph showing untreated sample of well-crystallized kaolinite.

K-WC
1500°C
3% O_2
2.9S

V-492a

FIGURE 7.7-7. - SEM micrograph showing kaolinite sample after processing at 1725 K in 3% O_2 for 2.9s.

To determine whether the composition of the montmorillonite sample was uniform, limited CCSEM analysis (100 particles) was conducted on the untreated sample. A ternary Ca-Al-Si diagram of the results of this measurement is shown in Figure 7.7-8. Note that a lack of ZAF correction for this sample results in an apparent high Al/Si ratio (relative to the bulk analysis in Table 7.7-1).

FIGURE 7.7-8. - Ca-Al-Si ternary diagram for unprocessed montmorillonite sample.

Experiments conducted with 38/53 μm montmorillonite (dry sieved) demonstrated a fairly rapid change in morphology upon exposure to a simulated combustion environment. Particles were initially of angular shape as seen in Figure 7.7-9. Silica-to-alumina ratios in these particles were approximately 3.5/1, with 10% of the particle composed of the modifier ions magnesium, calcium, and iron; most particles sampled were similar in composition to the bulk composition reported above. By way of comparison, the Silver Hill illite previously examined contained approximately 15 wt% of modifier ions (reported as oxides; Phase I Final Report). Subsequent to processing at 1500°C for 1s, vitrification was apparent in several of the particles as seen in Figure 7.7-10. After complete processing at 1500°C for 2.9s (similar to what minerals might encounter in a boiler environment), nearly complete melting was apparent (Figure 7.7-11).

7.7.1.3 Mineral Stickiness Testing

Deposit initiation (inertial impaction) experiments were conducted in the PSIT laminar flow reactor using isothermal tubes in crossflow as described in Subsection 7.2 of this report. Impaction velocities of 1 and 4 m/s were used at a range of gas temperatures.

FIGURE 7.7-9. - SEM micrograph of raw montmorillonite.

FIGURE 7.7-10. - SEM micrograph of montmorillonite after exposure to 3% O₂, 1500°C, 1s

FIGURE 7.7-11. - SEM micrograph of montmorillonite after exposure to 3% O₂, 1500°C, 2.9s.

In Phase II of this program, the first series of stickiness experiments were conducted with montmorillonite. Because of the high modifier ion content of the montmorillonite, sticky low-viscosity ash particles (capable of depositing over a wide range of conditions) were anticipated. Experiments were therefore conducted at impaction surface (and particle) temperatures of 1275 to 1675 K. Capture efficiencies of 40 to 50% for tube surface temperatures of 1300 K and above, comparable to those of the San Miguel lignite ash previously examined, were obtained. Detailed examination of the San Miguel lignite ash had indicated that calcium plus magnesium plus potassium levels of most particles were greater than 10% as oxides, by weight, yielding viscosities below the 10^7 Pa·s level believed necessary for adhesion (Boni et. al., 1990). This produced particles with viscosities low enough to permit the particle to remain on the impaction surface subsequent to contact, i.e., viscosities were low enough to absorb the energy of collision. For the calcium montmorillonite ash particles examined herein, the sum of the modifier ions calcium plus magnesium plus iron was in the range 6 to 12% for the individual particles studied (Table 7.7-2). Note that this range is comparable to the San Miguel ash particles so similar viscosities are expected.

For nominal 38/53 µm kaolinite samples, particle collection efficiencies (i.e., not corrected for impaction efficiency as a function of particle size) were less than 5% at all temperatures considered (maximum = 1725 K bulk gas temperature). This was expected, as no melting or vitrification was observed for samples K-WC and K-PC under all conditions examined. The limited amount of sticking which was observed was derived from molten

TABLE 7.7-2. - SEM/EDX analysis of Montmorillonite high-temperature deposit sample

	Montmorillonite	Deposit
SiO ₂	67.7	67.2
Al ₂ O ₃	19.7	19.9
TiO ₂	0.3	-
Fe ₂ O ₃	1.6	2.4
FeO	0.1	-
MgO	7.2	5.2
CaO	3.2	4.9
Na ₂ O	0.1	-
K ₂ O	0.2	0.5

illitic impurities in the kaolinite samples; these can be seen as circular molten droplets on the tube surface in Figure 7.7-12. Potassium levels of approximately 6% were observed in these regions.

To study the behavior of non-sticky ash particles in the presence of sticky ash particles, mixtures of kaolinite and montmorillonite in ratios of 50/50 and 25/75 by weight were tested. For the 25% kaolinite mixture, a collection efficiency of 38% was anticipated at 1625 K surface temperature, based upon an average of the two pure compound results. A collection efficiency of 65%, however, was observed, indicating incorporation of the non-sticky kaolinite particles into the deposit generated by the molten montmorillonite. For the 50/50 mixture, a collection efficiency of 28% was observed. This corresponds to an average of the individual montmorillonite and kaolinite capture efficiencies, suggesting limited interaction for this mixture. Based upon these results, it is speculated that erosion may become a factor at higher kaolinite percentages. Micrographs of these deposits are shown in Figures 7.7-13 and 7.7-14.

Experiments were also conducted with the nepheline samples described in the previous section of this report. Nepheline has been observed to form during combustion of a sodium-rich Beulah lignite; evidence suggesting formation of a potassium analog from potassium-rich coals was described in Subsection 4.5.5 of this report. Stickiness experiments conducted with the nepheline sample demonstrated limited melting (Figure 7.7-15) and low capture efficiencies at temperatures of 1475 K and below. Note that the particles collected in the sample shown in Figure 7.7-15 had a potassium oxide concentration of approximately 10%. As deposition surface (and local gas) temperature was increased to 1625 K, a significant increase in capture efficiency was noted. This can be seen in Figure 7.7-16, a comparison of sticking efficiencies for the mineral samples discussed in

K-WC
1350 to
1400°C
3% O₂

V-495a

FIGURE 7.7-12. - SEM micrograph of deposits derived from K-WC at a gas temperature of 1725 K, 3% O₂.

V-507

FIGURE 7.7-13. - SEM micrograph of K-WC/montmorillonite 25/75 deposit, 1625 K surface temperature.

V-498

FIGURE 7.7-14. - SEM micrograph of K-WC/montmorillonite 50/50 deposit, 1625 K surface temperature.

V-500

FIGURE 7.7-15. - SEM micrograph of nepheline deposits collected at a temperature of 1350°C.

1350°C

- more extensive
- some necking
- $T_m = 1526^\circ\text{C}$
- $\text{K}_2\text{O} \sim 10\%$

FIGURE 7.7-16. - Collection efficiencies of various Phase II mineral samples compared to San Miguel lignite.

this section of the report. Note that temperatures in this plot represent deposit tube temperatures, assumed to equal the local gas temperature measured via thermocouple in a non-particle flow experiment.

7.7.2 Stickiness Testing of Phase II Coals

Stickiness tests conducted with the beneficiated and low-ash Phase II coals yielded values considerably lower than for any of the Phase I U.S. coals at comparable conditions. Although low inertial impaction efficiencies, a result of the generally finer ash particle size distributions produced by these coals, were a contributing factor, the lack of significant calcium aluminosilicate formation kept absolute stickiness values low as well. Thus, the ash from these coals was (a) less likely to inertially impact, and (b) less likely to stick if it did impact.

The results for the Phase II coals are summarized in Table 7.7-3. A more detailed discussion of the testing of each coal follows.

7.7.2.1 Loy Yang 1953

The results of ash particle stickiness experiments conducted with LY 1953 are shown in Figure 7.7-17. In these experiments, oxygen levels of 7% were used at the highest temperature, and were increased as gas temperature was decreased to 12 and 16%, respectively, to maintain constant particle temperature (calculated using the model and results

TABLE 7.7-3. - Summary of stickiness testing results for Phase II coals.
lower tube (4 m/s) (wt% of ash)

	Deposit Surface Temperature (K)			
	1700	1650	1500	1375
Loy Yang 1953	50	10	0	8
Gravimelt 7A	30	-	-	-
Gravimelt 9C	10	-	4	-
I6 SOAP	15	8	-	4
Loy Yang 2301*	-	-	8	0
Kentucky #11*	-	-	25	-
Beulah*	-	-	42	-
*Phase I samples

FIGURE 7.7-17. - Collection efficiency measurements for Loy Yang 1953.

of Graham, 1991). Wall gas temperature is plotted on the x-axis; measured deposit tube surface temperatures are typically 75 to 100 K lower as discussed previously (Subsection 7.2). Note that these plots are uncorrected for impaction efficiency (i.e., no Stokes number correction applied) as the ash particle size distribution from CCSEM was not available. At high temperatures, a significant fraction of the ash passing through the cross-sectional area swept out by the impaction tube surface is captured, while at lower temperatures, levels of approximately 10% are observed. In previous experiments with LY 2301, a value of 8% was obtained at 1470 K, while values approaching 0 were obtained at 1350 K. Results from LY 1953 were therefore comparable.

7.7.2.2 Illinois #6 SOAP

Ash stickiness results for the SOAP coal are presented in Figure 7.7-18. Stickiness values for this coal were lower than those observed for any uncleaned bituminous coal previously examined, although a tenacious deposit has been observed from this coal in testing conducted elsewhere (Hurley et al., 1991). The chemical composition of three of these deposits, determined by SEMPC at UNDEERC, is given in Table 7.7-4. Iron concentrations were greatest in the deposit collected at the highest temperature, perhaps reflecting the increased iron-aluminosilicate interaction observed under those conditions.

FIGURE 7.7-18. - Collection efficiency, Illinois #6 SOAP

TABLE 7.7-4. - Illinois #6 SOAP deposit compositions by SEMPC

Combustion Conditions	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
1500°C 7% O ₂	34.8	20.0	36.5	2.2	1.7	0.7	0.6	3.3
1400°C 10% O ₂	45.3	20.4	23.7	2.0	2.7	1.1	0.6	4.1
1250°C 16% O ₂	46.8	20.3	21.4	2.4	3.6	1.4	0.7	3.2

7.7.2.3 Gravimelt 7A

Tests conducted with Phase I coals demonstrated a range of stickiness behavior, with stickiness being highest for coals containing calcium-rich aluminosilicate ash particles. A comparison of these results with those obtained for Gravimelt 7A at higher temperature is

shown in Figure 7.7-19. At a gas and tube surface temperature of 1425°C and a velocity of 4 m/s, 26% of those ash particles impacting the surface adhered. As the compositional analysis in Table 7.7-5 indicates, these particles were nearly identical in composition to the illite-derived ash particles observed in the combustion-generated ash sample. This suggests that illite-derived particles are the only ones sufficiently deformable to adhere to surfaces under these conditions. Pyrite does not appear to contribute to the formation of deposits for this coal. This is not surprising, as its low concentration and small diameter will promote rapid oxidation, leading to the formation of a few crystalline oxidized iron particles which will not deposit.

Analysis of the chemical composition of the deposit at various points along the surface, as determined by SEM-point count at the University of North Dakota, shows the spread of K-Al-Si compositions observed (Figure 7.7-20). This range corresponds closely to that observed previously for illite-derived ash particles (Phase I Final Report).

The viscosity of the average depositing particle composition was calculated from the model of Kalmanovitch and Frank (1990) using the relation

$$\mu = (AT) \exp(1000B/T)$$

where the constants A and B are functions of ash composition. In this model, iron must be defined as either FeO, a network former, or Fe₂O₃, an amphoteric; here it was considered to

FIGURE 7.7-19. - Comparison of collection efficiencies for program coals at 1500 K.

TABLE 7.7-5. - Gravimelt 7A ash and deposit chemical composition

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
7A (coal	49	11	15	5	8	2	3	7
PSIT ash	54	15	11	11	6	1	1	2
PSIT KY9 ash	56	19	16	1	4	0	0	4
Deposit 1	58	25	5	3	2	1	1	6
Deposit 2	56	25	7	3	2	1	1	5
Si-Al-K ash	55	30	3	2	0	0	1	6

*Overlapping Ba-energy counts excluded.

be in the fully oxidized state. At 1700 K, the temperature of the stickiness tests described above, the calculated viscosity for the composition of deposit 1 is 1.5×10^3 poise, well within the range for deposition of even the largest, highest velocity inertially impacting ash particles. At temperatures of 1200 K, however, the viscosity of this composition range has increased to 1.2×10^7 poise, which should be too high for ash particles of 20 μm and above to stick even at velocities as low as a few meters per second. Low temperature slagging is therefore not expected to be a severe problem with this coal, as the only sticky ash particles present - those derived from illite - will have viscosities approaching the critical range of 10^7 to 10^9 poise at this temperature. Note that the small size of the ash from this coal will result in small (relative to most coal ashes) particle kinetic energies, which *may* allow them to stick at these low temperature conditions. It is more probable, however, that these small ash particles will follow gas streamlines and not encounter wall surfaces directly.

7.7.2.4 Gravimelt 9C

Ash particle stickiness testing was also conducted with an unclassified Gravimelt 9C sample in air. Ash particle collection efficiencies measured for the as-received coal on an uncooled ceramic substrate were low at both conditions as shown in Table 7.7-6. Using the ash psd from the results of Subsection 7.3.5, an impaction efficiency of 25% (low velocity) results in an adhesion efficiency (collection/impaction) of only 15% at the higher temperature. The chemical composition of the adherent ash measured by SEM-point count (SEMPC) at UNDEERC was a mixture of aluminosilicates (Table 7.7-7). Note the absence of titanium in the deposit, suggesting that the titanium-rich particles formed during combustion were not sticky.

7.7.3 Acknowledgment for Subsection 7.7.1

The authors wish to acknowledge the assistance of Dr. R. Finkelman of USGS and Dr. P.J. Dunn of the National Museum of Natural History, part of the Smithsonian Institution, for their assistance in obtaining the nepheline sample.

(a) Run #1

(b) Run #2

FIGURE 7.7-20. - K-Al-Si Ternary diagram for Gravimelt 7A ash deposit obtained at 1425°C, 21% O₂.

TABLE 7.7-6. - Stickiness testing of Gravimelt 9C (as-received coal, 21% O₂)

T _{wall}	T _{combustion gas}	T _{dep'n surface}	Collection* η (1 m/s)	Collection* η (4 m/s)
1500°C	1450°C	1425°C	4.3	10.2
1300°C	1250°C	1225°C	2.7	4.2
*Impaction efficiency not incorporated				

TABLE 7.7-7. - Gravimelt 9C deposit composition 1500°C, 21% O₂
(coal - as received) (wt%)

SiO ₂	50.2
Al ₂ O ₃	36.7
Fe ₂ O ₃	3.5
TiO ₂	3.4
P ₂ O ₅	0.1
CaO	0.8
MgO	0.6
Na ₂ O	0.4
K ₂ O	4.3

7.8 Trace Element Transformations

To understand the fate of trace elements during coal combustion, several pieces of information must be obtained. These include the concentrations of the element in the coal, the forms of the element in the coal, the combustion transformations of the element, the dependence of these transformations on form, and the speciation of elements such as chromium between Cr III and Cr VI in the ash. In this preliminary study, we addressed several of these issues for a few of the elements listed as Hazardous Air Pollutants in the 1990 Amendments to the Clean Air Act. This was achieved through detailed characterization and laboratory experimentation with an Illinois 6 bituminous coal, a physically beneficiated Illinois 6, and the Phase I Beulah lignite coal.

7.8.1 Coal and Ash Analysis

The 1990 Amendments to the Clean Air Act identify 11 trace metals contained in coal that have been identified in power plant flue gases. Typical coal trace element concentrations for the 11 listed species are presented in Table 7.8-1. Data were taken from Finkelman (1992). Typical forms for these species, as adapted from Finkelman et.al. (1990) and Smith (1980), are presented in Table 7.8-2. For some of the elements, it is apparent that the exact form remains unknown. The efficiency of beneficiation in removing these elements prior to combustion therefore cannot be addressed adequately.

TABLE 7.8-1. - Concentrations of trace elements in U.S. coals

Element	Range - ppm in Coal	Mean (ppm)
Antimony	0.14 - 35	1.2
Arsenic	0.2 - 360	24
Beryllium	0.05 - 25	2.2
Cadmium	<0.02 - 100	0.5
Chromium	0.5 - 120	15
Cobalt	1 - 500	6.1
Lead	< 1 - 33	11
Manganese	1.4 - 4400	43
Mercury	0.01 - 8	0.2
Nickel	0.3 - 300	14
Selenium	0.5 - 150	2.8

TABLE 7.8-2. - Forms of trace elements in coal

Element	Form	% Organically Associated
Sb	Sulfides, organic	?
As	Sol'n in pyrite	40
Be	Clays, organic	(high)
Cd	Sphalerite	-
Cr	?	50
Co	Pyrite	40
Pb	Galena, PbSe	20
Mn	Clays	70
Hg	Sol'n in pyrite	-
Ni	?	70
Se	Pyrite, PbSe, organic	60

To assess the impact of coal beneficiation on the transformations of trace elements - i.e., those with concentrations typically $< 0.1\%$ in coal ash - the physically beneficiated Illinois 6 SOAP and its parent were analyzed by neutron activation analysis. Combustion experiments were then conducted at 1500°C , 10.5% oxygen, and the resulting ash was size-segregated with a cascade impactor and re-analyzed for chemical composition. Beulah lignite coal and ash products generated at 1500°C (wall temperature), 10.5% oxygen were also examined for comparison.

CCSEM mineral size distributions for these two coals are presented in Figure 7.8-1. A reduction in the mineral size distribution was clearly evident. This suggests that those trace elements associated with the larger minerals in the parent Illinois #6 would be removed more efficiently during beneficiation of this coal by the SOAP process. Neutron activation analysis of these coal and ash samples is presented in Tables 7.8-3 through 7.8-5. In each table, "coal" represents the elemental concentration within the coal (*not* within the coal ash), "TF" represents the concentration of each element in a total filter sample generated during combustion in the laboratory furnace, and "Top 3" represents the concentration in a sample collected on the top three stages of a Pollution Control Systems Corporation cascade impactor (i.e., $dp > 2.2\ \mu\text{m}$). For the Illinois 6 parent, As, Sb, and Th levels were depleted in the largest sizes, indicating concentration in the smallest ash particle sizes. For the SOAP, Zn, Cr (slight), As, Se, and Sb (slight) were all enriched in the smallest particle size range.

FIGURE 7.8-1. - CCSEM mineral size distributions for Illinois #6 Phase II parent and SOAP coals.

TABLE 7.8-3. - Trace element analysis, Illinois #6 Parent and ash (ppm, wt)

	ppm, wt		
	I6 Coal	I6 TF	I6 top 3
Sc	1.9	27	24
Cr	16	140	135
Co	13	200	180
Zn	22	210	170
As	1.5	11	5.6
Se	1.8	3.4	2.6
Sr	1	-	-
Cd	-	2.2	1.7
Sb	0.26	1.9	1.4
Cs	0.76	11	8.0
Th	1.3	55	17
U	2.1	10	10
Ti	450	5100	
% ash, I6 parent (as-received) 8.4 (dry basis) 9.4 % ash, I6 SOAP (as-received) 2.8 (dry basis 3.6) Fraction vaporized, parent $\approx$ 0.02 (est. from Phase I results) Fraction vaporized, SOAP $\approx$ 0.15			

TABLE 7.8-4. - Trace element analysis, Illinois 6 SOAP and ash

	ppm, wt			
	SOAP Coal	SOAP TF	SOAP top 3	SOAP bottom 3
Sc	1.4	46	44	4.3
Cr	16	290	440	530
Co	3.0	59	57	6.8
Zn	11	270	250	500
As	1.1	15	5.7	57
Se	1.3	13	5.6	13
Sr	-	130	245	-
Cd	-	4.2	-	3.9
Sb	0.28	3.0	1.5	11
Cs	0.41	6.4	5.0	9.6
Th	1.1	39	37	3.2
U	2.2	27	31	31
Ti	494	13500		
% ash, I6 parent (as-received) 8.4 (dry basis) 9.4 % ash, I6 SOAP (as-received) 2.8 (dry basis 3.6) Fraction vaporized, parent $\approx$ 0.02 (est. from Phase I results) Fraction vaporized, SOAP $\approx$ 0.15				

TABLE 7.8-5. - Trace element analysis, Beulah coal and ash

	ppm, wt		
	Beulah Coal	Beulah TF	Beulah top 3
Sc	1.2	21	20
Cr	3.0	46	70
Co	1.2	11	13
Zn	9.8	110	120
As	8.7	136	47
Sc	0.96	9.3	2.5
Sr	-	7700	5500
Cd	-	1.1	2.0
Sb	0.43	7.5	2.3
Cs	0.16	0.69	-
Th	1.5	26	26.0
U	0.68	9.1	8.1
Ti	228	-	-

Of interest is the change in concentration for several of the elements when the coal is beneficiated. Chromium, selenium, antimony, and uranium levels in the SOAP ash were all greater than in the parent coal ash, indicating that they were not removed as effectively as some of the major minerals. For the Beulah lignite, As, Se, and Sb were depleted in the largest particle sizes, suggesting enrichment in the submicron fraction of the ash for these elements.

This results are perhaps more easily understood when presented in graphical form, and clustered according to an element's response to beneficiation. First, consider elements effectively removed by the SOAP beneficiation process such as cobalt and zinc. In Figure 7.8-2, the results of combustion testing are presented for these two elements. For cobalt, the extensive reduction due to beneficiation results in a concentration in the SOAP ash lower than that in the parent coal ash. The non-volatile nature of this element leads to its being depleted in the finest ash sizes, as shown in the first part of the figure. For zinc, its relative volatility leads to an enrichment in the finest ash particle size fraction. Because it was removed to a lesser extent during beneficiation - 2x versus the 3x reduction in total ash content - its concentration in the SOAP ash is slightly higher than in the parent coal ash.

Next, consider elements removed slightly less efficiently in the beneficiation of this coal, such as arsenic and selenium. As the results in Figure 7.8-3 demonstrate, concentrations were higher in the SOAP ash than in the parent coal ash. The relative

FIGURE 7.8-2. - Concentrations of Co and Zn in laboratory combustion ash as a function of ash particle size.

FIGURE 7.8-3. - Concentrations of As and Se in laboratory combustion ash as a function of ash particle size.

volatility of both species, resulting in enrichment in the finest ash particle sizes, is also apparent. Similar results were obtained for selenium, as shown in Figure 7.8-4. Chromium, also shown in Figure 7.8-4, did not demonstrate the submicron enrichment of some of the other elements, but did demonstrate an increase in concentration in the ash as a result of relatively ineffective removal during coal beneficiation.

Thus, it can be concluded that elements not removed effectively by beneficiation will be significantly increased in concentration in the fly ash as a result of coal cleaning. As with the major inorganic species in coal, the ability of beneficiation to remove an element depends strongly on the form of that element in the coal. To predict the effects of beneficiation on trace element removal, therefore, a better understanding of the forms of these elements in coals is required.

FIGURE 7.8-4. - Concentrations of Sb and Cr in laboratory combustion ash as a function of ash particle size.

7.8.2 XAFS Analysis - Chromium

One of the potentially hazardous elements on the Clean Air Act "Air Toxics" list is chromium. While chromium present in the +3 oxidation state is relatively benign in sub-

100 ppm concentrations (Tietz, 1990), chromium as chromate (CrO_4^{2-} , i.e., +6 Cr) is toxic and carcinogenic. For utility pulverized coal combustion, therefore, knowledge of both the *amount* and the *form* of chromium in the coal and in the combustion-generated ash is extremely important. A typical chromium concentration in U.S. coal is 15 to 20 ppm [Finkelman, 1992; Raask, 1985], with values as high as 250 ppm reported [Finkelman, 1992]. Higher concentrations of chromium are reported in the earth's crust (100 ppm) than in coal [Smith, 1980]. It has been reported that chromium concentration increases with increasing rank for the series sub-bituminous, bituminous, anthracite [Brooks, 1989; Raask, 1985]. There is a discrepancy in values reported for lignitic coals, however; Raask [1985] reports concentrations comparable to anthracite, while Brooks [1989] reports levels lower than sub-bituminous coals. These findings are summarized in Table 7.8-6. The *forms* of chromium contained in coal are still largely uncertain. Finkelman [1992] suggested that chromium oxide or chromite and chromium contained within clays are both possibilities. Smith [1980] indicated that up to 50% organic association may be possible. This uncertainty is in part due to the use of indirect methods for determining elemental forms.

TABLE 7.8-6. - Chromium concentrations in coals of different rank

	Raask [1985]	Brooks [1989]
Lignite	20 ppm	13.5 ppm
Sub-bituminous	7	14.9
Bituminous	15	20.5
Anthracite	20	47.9

X-ray absorption fine structure (XAFS) spectroscopy has demonstrated potential for investigating the forms of occurrence of trace elements [Huggins et al., 1989; Wong et al., 1984. See also Subsection 4.5.8.7 of this report). This technique has the ability to focus on a specific element in a material and to provide detailed information relevant to the local bonding and structure of the element in the material, from which the form of occurrence can usually be deduced. Furthermore, this technique is both direct and non-destructive.

XAFS spectroscopy on coal and ash samples was therefore performed by the University of Kentucky at beam-line X-19A at the National Synchrotron Light Source, Brookhaven National Laboratory. For trace amounts of chromium in coals and ash samples, the absorption of X-rays was measured over the spectral range from 5.9 to 6.2 keV; over the X-ray absorption near-edge structure (XANES) region (5.97 to 6.03 keV), absorption data were collected every 0.2 eV. Absorption of the X-rays for trace chromium samples was measured by means of a thirteen-element germanium array detector [Cramer et al., 1988] that detected the fluorescent X-rays only in a specified tunable energy window that corresponded to the energy of the chromium fluorescent K_{α} X-rays. In addition, a 6μ vanadium filter was used to minimize background. Up to ten scans were recorded and

summed for the weakest absorbers. The spectral summations, the pulse-height windowing, and the low-energy filtering all contributed to enhance the signal-to-noise ratio of the trace element spectra. For reference standards, conventional ion chambers were used to measure both the fluorescent and absorption XAFS spectra in a single scan. For many of the trace chromium coals and ash samples, the chromium EXAFS region was terminated by a surprisingly strong Ce L_{II} absorption edge at about 175 eV above the Cr K edge, which effectively made the EXAFS region uninformative. The zero energy point (5.989 keV) for chromium was defined as the first inflection point in the XAFS spectrum of chromium metal foil.

As discussed above, although beneficiation reduced the ash content of the Illinois #6 coal from 9.3 to 3.6% (dry basis), chromium concentrations in the coal remained unchanged at 16 ppm. The chromium concentration in the combustion derived ash was therefore expected to be approximately 2.5 times greater when the beneficiated Illinois #6 was burned. Measured concentrations in the beneficiated coal ash were approximately twice as large as those in the ash from the parent coal. Values as high as 300 to 400 ppm in the ash were observed. For the cleaned coal, a slight increase in concentration was noted with decreasing particle size. The magnitude of the size-dependent change is, however, within experimental uncertainty.

Because the concentration of chromium in the coal remained unchanged upon beneficiation, its presence in very small minerals or as an organically associated substance is indicated. It is likely not present as a substitutional element in clays, as large clay minerals were effectively removed by cleaning.

It is a relatively easy matter to discriminate by means of XAFS spectroscopy among the two most common oxidation states of chromium, Cr^{3+} and CrO_4^{2-} , found in natural and environmental samples. Chromium XAFS spectra of two chromic oxide and two chromate samples are shown in Figure 7.8-5. The chromate oxidation state is characterized by the presence of a large pre-edge feature at about 0 eV that is highly distinctive of first series transition metal $3d^0$ species in tetrahedral coordination by oxygen anions. In addition, it should be noted that the maximum absorption in the chromate species occurs at about 40 to 50 eV, at which energy a minimum in the absorption occurs for the Cr^{3+} compounds. These observations appear to be quite general and to apply to all the chromium standards so far examined.

Figure 7.8-6 shows chromium XAFS spectra obtained for Illinois #6 coal and ash samples. The spectra of the parent and the cleaned product are virtually identical in appearance and clearly demonstrate that all (>95%) of the chromium is present in the Cr^{3+} oxidation state. This suggests that there is only one significant chromium form of occurrence and that it is not strongly associated with the mineral matter, otherwise the chromium abundance would have dropped significantly upon cleaning and the XAFS spectrum would have shown significant variation. Chromium in the ash sample is also predominantly Cr^{3+} , although the spectral shape differs somewhat from that of the coal samples.

FIGURE 7.8-5. - Chromium K-edge XANES spectra of two chromic and two chromate oxide reference standards, as determined by the University of Kentucky.

FIGURE 7.8-6. - Chromium K-edge XANES spectra of Illinois #6 Phase II parent coal, SOAP beneficiated coal, and a combustion-derived ash sample, as determined by the University of Kentucky.

7.9 Development of an Engineering Model for Ash Particle Size and Composition

During Phase II, a model capable of predicting fly ash formation during pulverized coal combustion was developed. Using coal particle size distributions, coal mineralogy composition distributions, mineral size distributions, bulk ash content, volatile fraction, and swelling indices as inputs, the model uses rules based upon fundamental interactions observed in the experimental portion of this program to generate ash particle size and chemical composition distributions. This latter feature is a unique aspect of this model. In addition, it is the only model accounting for particle-to-particle variations in mineral content, size, and composition. It thus provides a numerical analog of physical reality in simulating fly ash generation. Phenomena such as char fragmentation and partial coalescence are also included using models developed during Phases I and II of this program. The development of the Engineering Model has been described in several program quarterly reports and in a recent paper (Wilemski et al., 1991); these documents are combined herein to provide a comprehensive description of the model.

7.9.1 Background

Indices of slagging and fouling are often based on an estimate of the viscosity of ash. The viscosity is considered to be a key parameter affecting both the sticking probability of ash impacting on surfaces and the strength of any deposit formed. Several approximate indices are based on the base/acid ratio (b/a) calculated from the mean composition of coal ash, and defined as the ratio of the weight percent in the coal ash of base oxides ($\text{FeO} + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) to acid oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$). Examples of some uses of the base/acid ratio are: 1) for bituminous coals, values of (b/a) above 0.5 are indicative of a propensity to foul and values below 0.27 are considered to give ashes too viscous for use in slagging cyclone burners; 2) (b/a) multiplied by the weight percent sodium oxide defines a fouling index R_f ; values of $R_f < 0.2$ suggest that the potential for fouling is low whereas $R_f > 1.0$ implies that the potential for fouling is severe; and 3) (b/a) multiplied by the weight percent sulfur defines a slagging index R_s ; the potential for slagging is considered to be low for $R_s < 0.6$ and severe for $R_s > 2.6$ (Raask, 1985). Indices are expected to be of greater value when the property of concern is well represented by the mean composition, e.g., the fluidity of an ash deposit, but not when it depends upon individual particle behavior, e.g., the sticking coefficient on a clean tube.

It has long been recognized that the composition of ash varies widely from particle to particle. Today, this variation can be readily measured using computer controlled scanning electron microscopy (CCSEM), which permits the rapid determination of the composition of statistically significant numbers of ash particles. For purposes of estimating the fouling potential of coals before they are burned, however, it is desirable to relate the variability of the ash composition to indices that can be evaluated from analyses made on unburned coal. A useful starting point in the development of such indices is the composition and size distribution of mineral inclusions in the coal determined by CCSEM.

Ash particles are produced by transformations and interactions of these mineral inclusions during combustion. Two limiting cases will be considered. In the first, each mineral inclusion is assumed to produce one ash particle (no coalescence). In the second, the minerals in each coal particle are assumed to coalesce during char burnout so that one ash particle is produced (full coalescence). In either case, extraneous minerals are assumed to produce one ash particle per mineral. Organically associated species are assumed to coalesce with the included ash, with the amount adding to any particular ash particle proportional to the surface area of that particle. Which of the above limiting cases applies depends on the mineral transformations and the level of char fragmentation during burnout. Formation of a single ash particle per mineral inclusion is favored by extensive char fragmentation during burnout, high melting point mineral inclusions that do not coalesce, or both. Factors that enhance char fragmentation are high char porosity, low ash content, and large particle size.

In the absence of char fragmentation, and for ash inclusions with a low melting point, the mineral content in a coal particle will end up in a single ash particle, the composition of which will be determined by those of the mineral inclusions of the parent coal particle. In principle, the mineral content of each coal particle can be determined by CCSEM. The effort required, however, is large and would need to be repeated for every coal grind. An alternative is to evaluate the mineral inclusion compositions and sizes once for any coal with CCSEM, and to use a mineral redistribution model to determine how the minerals are distributed among particles for any coal grind. The results of such an analysis are described in this section, and compared to the resultant distributions of ash composition and size for the full coalescence model and the experimental data.

7.9.2 Mineral Distribution Models

CCSEM analyses usually assign minerals found in a coal to one of a number of classes based on their elemental composition and further subdivide these into a number of size ranges. The analyses for this study were performed by Huffman and Huggins at the University of Kentucky and reported in the Phase I Final Report (Boni et al., 1990). They used six size ranges (<2.5 , 2.5 to 5, 5 to 10, 10 to 20, 20 to 40, and >40 μm) and six or seven composition classes (quartz, kaolinite, illite or montmorillonite, mixed silicates, pyrite, occasionally calcite, and the residual). These minerals, so classified, need to be distributed into the coal particles to provide a measure of the variation of the amount and composition of minerals among particles and of the extraneous ash. Several models for this purpose have been developed recently, as described below.

7.9.2.1 Monte Carlo Simulation

In this method (Charon et al., 1990), the coal particle size distribution is first subdivided into a number of size ranges. The mineral particles are distributed, one by one, into randomly selected coal particles while keeping track of the composition and amount of minerals accumulated in each coal particle. If the volume of a mineral particle exceeds the mineral-free volume of the selected coal particle, it is treated as extraneous. This procedure is straightforward, but computationally expensive, since large numbers of both mineral and

coal particles must be used to ensure the inclusion of a statistically significant number of larger particles. For example, subdivision of the coal size distribution into seventeen size bins from 10 to 170 μm involved 800,000 coal particles; placing the minerals into six size bins from 1 to 60 μm for each of six composition classes required 27,000,000 particles (Charon et al., 1990).

7.9.2.2 Poisson Distribution

Barta et al. (1990) used Poisson distribution functions and their transforms to represent the distribution of the mineral particles in coal. These techniques are valid approximations considering the large numbers of particles involved. For example, for m monodisperse mineral inclusions in n coal particles, the probability of finding a coal particle with j mineral inclusions can be approximated by

$$P_j = \lambda^j e^{-\lambda} / j!$$

where $\lambda = m/n$. By use of Fourier transforms, this distribution can be extended to a range of coal and mineral sizes (Barta et al., 1990) to calculate the mean and variance of the content and composition of the different coal particle sizes. The analysis, however, breaks down for cases in which the mineral particles occupy a significant fraction of a coal particle's volume and provides no estimate of the amount, size, and composition of the extraneous mineral matter.

7.9.2.3 Composite Method

This approach is an alternative to the Monte Carlo method that is well suited for computers with modest speed and storage capabilities. It treats the distribution of mineral particles among the smallest coal particles by means of Poisson distributions. The mineral redistribution among the larger coal particles is performed in a way similar to the full Monte Carlo method for the larger mineral particles, but the smallest inclusions are treated on an average basis. The rationale for these differences is to reduce the computer memory and time requirements to a reasonable level.

Typically, a simulated coal particle size distribution (psd) will contain several hundred thousand particles of the smallest size (10 μm) and about forty thousand particles of all larger sizes ($\geq 20 \mu\text{m}$). These numbers insure that at least one or two coal particles are present in each of the largest size ranges of the coal psd. The simulated mineral psds consist of several million inclusions of the smallest size (2 μm) and several hundred thousand of all of the larger sizes ($\geq 4 \mu\text{m}$). Examples of these distributions are shown in Table 7.9-1 for an Illinois #6 coal.

The slowest part of the Monte Carlo method is the distribution of the smallest mineral particles; the largest memory requirements arise in treating each of the smallest coal particles individually. Therefore, in the composite method, the Monte Carlo method is used only for the larger mineral and coal particles (all sizes except the smallest, most numerous). In this

way, it is possible to efficiently distribute the several hundred thousand larger mineral particles among the roughly forty thousand larger coal particles without exceeding the virtual memory limit of the computer system. Typical execution times for this process are 5 to 10 cpu minutes on a DEC Microvax II. Similar memory and speed constraints hold for 386-based PC systems.

To save execution time, the smallest ($2\text{ }\mu\text{m}$) mineral particles are distributed among the large coal particles on an average basis. These inclusions are found in large numbers in each large coal particle. Therefore, no serious error is incurred by neglecting fluctuations and assigning the number to each particle in direct proportion to its mineral free volume. To make further significant reduction of the required computer memory, the smallest ($10\text{ }\mu\text{m}$) coal particles are divided into classes whose size and mineral content are determined using Poisson distributions as explained below.

The complete mineral redistribution procedure in the Composite Method is outlined on the flow chart in Figure 7.9-1. The procedure has five principal components:

- (1) Discrete representations of the coal and mineral psd's are first generated using measured values.
- (2) Randomly selected large mineral particles ($> 2\text{ }\mu\text{m}$) are placed in randomly chosen large coal particles ($> 10\text{ }\mu\text{m}$) via the Monte Carlo procedure outlined earlier. Average numbers of $2\text{ }\mu\text{m}$ mineral particles are then added to each particle as described above. The full mineral inventory of every large coal particle is saved.
- (3) If the selected coal particle lies in the $10\text{ }\mu\text{m}$ size range, all mineral particles larger than $8\text{ }\mu\text{m}$ are automatically excluded. All 4 and $8\text{ }\mu\text{m}$ mineral particles are initially assumed to fit into the coal particles, but records of the compositions of the minerals accumulating in individual $10\text{ }\mu\text{m}$ coal particles are not saved. Only the total numbers of 4 and $8\text{ }\mu\text{m}$ particles of each mineral type placed are stored. After placement of all the large mineral particles is completed, the Poisson probability distribution is used to partition the $10\text{ }\mu\text{m}$ coal particles into a number of classes whose specific mineral content is saved. The classes comprise groups of coal particles containing: 1) no 4 or $8\text{ }\mu\text{m}$ mineral particles; 2) one $4\text{ }\mu\text{m}$ mineral; 3) one $8\text{ }\mu\text{m}$ mineral; 4) two $4\text{ }\mu\text{m}$ minerals; and 5) one 4 and one $8\text{ }\mu\text{m}$ mineral. These represent the most probable possibilities; in addition the number of excluded $8\text{ }\mu\text{m}$ particles is estimated using the Poisson distribution.
- (4) The smallest ($2\text{ }\mu\text{m}$) mineral particles are distributed among the $10\text{ }\mu\text{m}$ coal particle classes thereby generating numerous subclasses. Poisson statistics, as described below, are used to determine the fractions of each class receiving a specific number of particles of each mineral type per coal particle.
- (5) After all of the discrete inclusions have been distributed, the organically bound inorganic species are distributed in direct proportion to the mineral-free volume of each coal particle.

TABLE 7.9-1. - Simulated coal and mineral particle distributions for Illinois #6

Coal Particle Size Distribution						
Average Size (μm)	Input		Output			
	Volume Frac. (%)	Number Frac. (%)	Number	Volume Frac. (%)		
10.00	16.10	81.571	154984	16.23		
20.00	22.20	14.060	26713	22.38		
30.00	14.70	2.758	5241	14.82		
40.00	12.30	0.974	1850	12.40		
50.00	8.30	0.336	639	8.36		
60.00	6.40	0.150	285	6.45		
70.00	5.20	0.077	146	5.24		
80.00	3.20	0.032	60	3.22		
90.00	2.40	0.017	32	2.44		
100.00	2.00	0.010	19	1.99		
110.00	1.60	0.006	12	1.67		
120.00	1.20	0.004	7	1.27		
130.00	0.50	0.001	2	0.46		
140.00	1.20	0.002	4	1.15		
150.00	1.00	0.002	3	1.06		
160.00	1.00	0.001	2	0.86		
Number of Inclusions of Each Size (μm) for Each Mineral Type						
Mineral	2.0	4.0	8.0	16.0	30.0	60.0
Quartz	215389	40986	4543	543	19	0
Kaolinite	98826	13345	995	155	5	0
Illite	201330	22041	2023	133	8	0
Mix. Sil.	306030	37131	3258	306	16	2
Pyrite	76525	6407	1168	568	81	5
Calcite	22255	3019	363	197	24	5
Others	102037	1697	272	336	68	4
All min.	1022392	124626	12622	2238	221	16

The redistribution of mineral inclusions among the smallest coal particles ($10\ \mu\text{m}$) is performed with Poisson distributions whose use is justified by the following statistical characteristics: (1) There are a large number of trials, N_i , equal to the number of mineral particles of each type. (2) There is a small probability p_α of successfully placing a single mineral particle of any type in any particular coal particle. This probability is the ratio of the mineral-free volume V_α of a $10\ \mu\text{m}$ coal particle to the total mineral-free volume V_T of the entire sample distribution, $p_\alpha = V_\alpha/V_T$. There are different values for p_α depending on whether the $10\ \mu\text{m}$ coal particle contains any 4 and/or $8\ \mu\text{m}$ mineral inclusions. (3) The

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FIGURE 7.9-1. - Flow chart for stochastic fly ash formation code.

average number $\lambda_{i\alpha}(=N_i p_{i\alpha})$ of mineral particles of type i in a $10\text{ }\mu\text{m}$ coal particle is small. The average number of $2\text{ }\mu\text{m}$ mineral particles (of all types) is generally in the range of 1 to 5. The average number of 4 or $8\text{ }\mu\text{m}$ particles is much less than one.

With these definitions, the probability of finding k_i small mineral particles of type i in a particular coal particle is given by the familiar expression

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

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

For each of the classes of $10\text{ }\mu\text{m}$ coal particles, a set of P_T values is generated by varying the k_i values from 0 to some modest upper limit k_m . To date, the value $k_m = 4$ has been found to give satisfactory results. Combinations of k_i values that yield $P_T < 0.001$ are not saved but are lumped together for eventual averaging. The surviving combinations plus the average of all the rejected ones comprise a set of subclasses into which the original number of coal particles in the category have been subdivided. The number of particles in each subclass and the associated mineral composition are stored to await processing into ash particles after distribution of the organically bound inorganic matter.

7.9.2.4 Ash Formation and Analysis

With a complete inventory available for the mineral content of each coal particle in the simulated coal psd, the model can be used to predict the composition and size distributions of the ash produced during combustion. The ash particles generated by treating the coal particles in the two limits of full coalescence and no coalescence are statistically analyzed to produce the modeling results described in the following sections. Additional discussion in latter sections describes char fragmentation modeling and the impact of limited coalescence.

Sample mineralogical results, shown in Table 7.9-2, form the basis for analyzing the flyash particle distribution according to elemental composition and particle size. The flyash analysis is performed for the full set of flyash particles and for a randomly selected subset of particles used with auxiliary routines for plotting triangular composition diagrams. The analysis produces a classification of the flyash particles into categories based on the concentrations of up to three elemental species. For each category the analysis also produces the number average and volume average compositions and the area percent of the category in the entire sample. For the major categories as determined by area percent, size distributions in terms of area percent and number percent are computed. These size distributions are also computed for the entire sample. Number percents for the major

Table 7.9-2. Mineral inventory of some selected fly ash particles

Particle Number	Particle Volume	Volume of Each Mineral Type						
		Quartz	Kaolinite	Montmor.	Mix. Sil.	Pyrite	Others	CaO-org. bd
1	137	68	0	9	7	0	1	52
2	99	2	0	4	67	0	1	25
3	73	4	0	9	7	0	1	52
4	137	68	0	9	7	0	1	52
5	708	68	0	521	70	0	1	48
6	137	4	0	9	71	0	1	52
7	137	68	0	9	7	0	1	52
8	201	4	0	73	71	0	1	52
9	201	68	0	9	71	0	1	52
10	201	68	0	73	7	0	1	52
24974	2519	223	0	643	1266	0	8	379
24975	2816	1235	0	168	670	0	517	226
24976	2901	287	0	1219	1010	0	8	377
24977	3128	161	0	839	1205	0	521	402
24978	2077	223	0	68	1395	0	9	382
24979	2208	81	0	548	1371	0	5	203
24980	3941	156	0	1661	1261	0	520	343
24981	4041	1246	0	1153	753	0	520	369
24982	1978	271	0	671	855	0	4	177
24983	2583	159	0	1091	946	0	8	379
25835	9408	1053	0	1224	5846	0	153	1132
25836	14757	3047	0	4829	5541	0	92	1248
25837	8644	1377	0	2577	3420	0	90	1180
25838	8916	2327	0	571	4940	0	24	1054
25839	9209	1482	0	3423	3383	0	20	901
25840	6767	1259	0	1254	2412	0	541	1301
25841	12115	3716	0	1810	5678	0	83	828
25842	8036	619	0	2149	2923	0	1053	1292
25843	9439	1164	0	1444	5819	0	85	927
25844	8805	2189	0	1509	4155	0	21	931

categories are also found. The form of the results is such that it permits direct comparison with the experimental CCSEM data originating at the University of Kentucky. Examples of the flyash analysis output are shown in Tables 7.9-3, 7.9-4, 7.9-5, and 7.9-6. As a test case, these results were generated using a limited coalescence option that prevented any 16, 30, or 60 μm inclusions from coalescing with any smaller inclusions.

7.9.3 Simulation Results

In this section, predicted ash composition and size distributions are compared with experimental data for four coals: Illinois #6, Kentucky #11, Upper Freeport, and San Miguel Lignite. The model predictions were made using the composite mineral redistribution method with the measured coal and mineral psds shown in Figure 7.9-2 and Table 7.9-7. Each coal will be discussed separately.

The experimental data with which the calculated results are compared were obtained in two reactor facilities at PSI Technology (PSIT) and the University of Arizona (UA) respectively. At PSIT, experiments were conducted in a methane flame pre-fired, drop-tube furnace. Residence times in this furnace were about 1 to 3s and gas temperatures ranged from 1500 to 1750 K. Oxygen concentrations were varied between 7 and 21%. At University of Arizona, combustion occurred in a self-sustained laboratory down-flow combustor of nominal 60,000 to 100,000 Btu/hr scale. About 20% excess air was used in these experiments. In all cases, UA impactor stage 1 sample data were used for comparison. Detailed descriptions of the operating characteristics of each facility are presented elsewhere (Subsections 6.1 and 7.2 of this report).

7.9.3.1 Kentucky #11

Figure 7.9-3 shows triangular composition plots of the minerals, measured ash, and full coalescence model predictions for silicon, aluminum, and iron containing minerals. The experimental results show that pyrite and aluminosilicate minerals coalesce during combustion. This trend is well represented by the model except for a modest deficiency in the predicted Al content. The results also show that the ASTM ash composition does not adequately represent the wide variability in the measured ash composition. A breakdown of the ash composition by major categories is shown in Figure 7.9-4. The full coalescence model predictions agree well with the Arizona and PSIT experimental results except for the iron aluminosilicates (SiAlFe), which are overpredicted. The no coalescence model overpredicts the amounts of quartz (Si), pyrite (Fe), and illite (SiAlK), and fails to predict any iron aluminosilicate. This is consistent with significant coalescence occurring for these minerals. The ash psd is shown in Figure 7.9-5. The full coalescence model provides a good description for ash below 15 μm , while limited coalescence is implied for particles above this size. The prediction of the no coalescence model is significantly finer than what is measured; thus, coalescence occurs to a significant extent for the minerals in this coal.

TABLE 7.9-3. - Elemental composition and area percent of full computer-generated fly ash sample for San Miguel Lignite based on limited coalescence of 16, 30, and 60 μ m minerals

#	Species	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cu	Area %
Number Average Elemental Composition														
5367	Si Ca -	0	0	4	58	0	1	0	2	33	1	1	0	4.4
4826	Ca Si -	0	0	3	17	0	1	0	1	76	0	0	0	1.7
4174	Si Al Ca	0	0	13	68	0	1	0	4	11	1	1	0	7.3
3631	Ca Si Al	0	0	8	39	0	1	0	3	47	0	1	0	2.0
6793	Si Ca Al	0	0	10	59	0	1	0	3	24	1	1	0	10.9
1873	Si - -	0	0	4	86	0	1	0	2	4	1	1	0	9.7
180	Si Ca S	0	0	10	53	0	11	1	1	19	5	1	0	0.3
1559	Si Al -	0	0	17	71	0	2	1	3	3	2	1	0	12.3
15	Si S Ca	0	0	10	56	0	13	1	1	12	5	1	0	0.0
326	Si S Al	0	0	11	57	0	15	1	1	8	6	1	0	2.8
1	Si Al S	0	0	13	63	0	8	1	2	8	4	1	0	0.0
39	Fe Si -	0	0	2	15	0	0	0	0	3	5	75	0	0.6
5136	Si Al K	0	0	14	75	0	1	0	6	2	0	1	0	48.1
33920	Totals	0	0	9	56	0	1	0	3	28	1	1	0	100.0
Volume Average Elemental Composition														
5367	Si Ca -	0	0	4	66	0	1	0	2	25	1	1	0	4.4
4826	Ca Si -	0	0	3	18	0	1	0	1	77	0	0	0	1.7
4174	Si Al Ca	0	0	13	68	0	1	0	4	11	1	1	0	7.3
3631	Ca Si Al	0	0	8	40	0	1	0	3	48	0	1	0	2.0
6793	Si Ca Al	0	0	10	64	0	1	0	4	19	1	1	0	10.9
1873	Si - -	0	0	3	90	0	1	0	2	2	1	1	0	9.7
180	Si Ca S	0	0	10	54	0	12	1	1	18	5	1	0	0.3
1559	Si Al -	0	0	19	69	0	2	1	3	3	2	1	0	12.3
15	Si S Ca	0	0	10	57	0	13	1	1	12	5	1	0	0.0
326	Si S Al	0	0	11	57	0	15	1	1	8	6	1	0	2.8
1	Si Al S	0	0	13	63	0	8	1	2	8	4	1	0	0.0
39	Fe Si -	0	0	2	15	0	0	0	0	3	5	75	0	0.6
5136	Si Al K	0	0	14	76	0	1	0	6	2	0	1	0	48.1
33920	Totals	0	0	13	73	0	2	0	5	5	1	2	0	100.0

TABLE 7.9-4. - Size distributions for full computer-generated fly ash sample for San Miguel Lignite based on limited coalescence of 16, 30 and 60 μ m inclusions

Species			Size (μ m)	1.0	4.0	8.0	16.0	30.0	60.0	> 80.0
Size Distribution for Each Fly Ash Type (area % for each fly ash type)										
Si	Al	Ca	7.27	0.00	0.00	78.54	21.11	0.35	0.00	0.00
Si	Ca	Al	10.91	0.00	2.94	49.16	29.37	13.86	4.67	0.00
Si	-	-	9.67	0.00	0.21	9.57	47.15	32.13	10.95	0.00
Si	Al	-	12.33	0.00	0.41	0.45	47.95	34.02	17.16	0.00
Si	Al	K	48.08	0.00	0.00	0.08	44.51	40.64	14.78	0.00
Others			11.74	0.00	15.58	54.83	15.43	5.15	9.01	0.00
Totals			100.00	0.00	2.22	18.53	38.42	28.98	11.85	0.00
Size Distribution for Each Fly Ash Type (number % in each fly ash type)										
Si	Al	Ca	12.31	0.00	0.00	85.15	14.83	0.02	0.00	0.00
Si	Ca	Al	20.03	0.00	10.53	76.17	11.48	1.71	0.12	0.00
Si	-	-	5.52	0.00	3.20	30.22	57.02	8.81	0.75	0.00
Si	Al	-	4.60	0.00	9.62	2.44	71.91	14.24	1.80	0.00
Si	Al	K	15.14	0.00	0.00	0.53	77.51	20.13	1.83	0.00
Others			42.41	0.00	35.78	61.44	2.46	0.22	0.10	0.00
Totals			100.0	0.00	17.90	53.65	23.36	4.63	0.47	0.00

To explore the sensitivity of the results to charges in the parent coal particle size distribution, simulations were also conducted with the fine coal PSD's shown in Figure 7.9-6. Results from coal distribution #1, shown in Figure 7.9-7, and from coal PSD Fine #2, shown in Figure 7.9-8, demonstrate sensitivity to coal PSD. This implies that an accurate measurement of the coal particle size distribution is important for accurate prediction of the final ash particle size distribution.

7.9.3.2 San Miguel Lignite

Figure 7.9-9 contains triangular composition plots of the minerals, measured ash, and full coalescence model predictions for silicon, aluminum, and calcium containing minerals. The experimental results show that organically-bound calcium and aluminosilicate minerals

TABLE 7.9-5. - Elemental composition and area percent of randomly selected subset of computer-generated fly ash particles for San Miguel Lignite based on limited coalescence of 16, 30, and 60 μ m inclusions

#	Species	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cu	Area %
Number Average Elemental Composition														
143	Si Ca -	0	0	4	57	0	1	0	2	34	1	1	0	3.8
142	Ca Si -	0	0	3	17	0	1	0	1	76	0	0	0	1.7
122	Si Al Ca	0	0	13	68	0	1	0	4	11	1	1	0	7.8
105	Ca Si Al	0	0	8	39	0	1	0	3	47	0	1	0	2.0
213	Si Ca Al	0	0	10	59	0	1	0	3	24	1	1	0	11.1
53	Si - -	0	0	4	86	0	1	0	2	4	1	1	0	11.7
4	Si Ca S	0	0	9	50	0	11	1	1	22	4	1	0	0.2
52	Si Al -	0	0	18	71	0	2	1	3	3	2	1	0	13.3
0	Si S Ca	0	0	0	0	0	0	0	0	0	0	0	0	0.0
7	Si S Al	0	0	11	57	0	15	1	1	8	6	1	0	1.3
0	Si Al S	0	0	0	0	0	0	0	0	0	0	0	0	0.0
1	Fe Si -	0	0	2	15	0	0	0	0	3	5	75	0	0.2
155	Si Al K	0	0	14	75	0	1	0	6	2	0	1	0	46.9
997	Totals	0	0	9	56	0	1	0	3	28	1	1	0	100.0
Volume Average Elemental Composition														
143	Si Ca -	0	0	4	64	0	1	0	2	27	1	1	0	3.8
142	Ca Si -	0	0	3	19	0	1	0	1	76	0	0	0	1.7
122	Si Al Ca	0	0	12	70	0	1	0	4	10	1	1	0	7.8
105	Ca Si Al	0	0	8	40	0	1	0	3	48	0	1	0	2.0
213	Si Ca Al	0	0	10	64	0	1	0	4	19	1	1	0	11.1
53	So - -	0	0	3	91	0	1	0	2	1	1	1	0	11.7
4	Si Ca S	0	0	9	54	0	11	1	1	18	5	1	0	0.2
52	Si Al -	0	0	18	70	0	2	1	3	3	2	1	0	13.3
0	Si S Ca	0	0	0	0	0	0	0	0	0	0	0	0	0.0
7	Si S Al	0	0	11	57	0	15	1	1	8	6	1	0	1.3
0	Si Al S	0	0	0	0	0	0	0	0	0	0	0	0	0.0
1	Fe Si -	0	0	2	15	0	0	0	0	3	5	75	0	0.2
155	Si Al K	0	0	14	76	0	1	0	6	2	0	1	0	46.9
997	Totals	0	0	12	76	0	1	0	5	4	1	1	0	100.0

TABLE 7.9-6. - Size distributions for randomly selected subset of computer-generated fly ash particles for San Miguel Lignite based on limited coalescence of 16, 30 and 60 μ m inclusions

Species	Size (μ m)	1.0	4.0	8.0	16.0	30.0	60.0	> 80.0
Size Distribution for Each Fly Ash Type (area % for each fly ash type)								
Si Al Ca	7.84	0.00	0.00	72.10	17.07	10.84	0.00	0.00
Si Ca Al	11.10	0.00	2.74	51.18	31.97	14.11	0.00	0.00
Si - -	11.68	0.00	0.00	8.75	36.53	32.84	21.89	0.00
Si Al -	13.30	0.00	0.00	0.68	56.06	43.26	0.00	0.00
Si Al K	46.92	0.00	0.00	0.19	48.04	35.42	16.35	0.00
Others	9.16	0.00	19.78	61.34	18.88	0.00	0.00	0.00
Totals	100.00	0.00	2.12	18.16	40.88	28.62	10.23	0.00
Size Distribution for Each Fly Ash Type (number % in each fly ash type)								
Si Al Ca	12.24	0.00	0.00	85.25	13.93	0.82	0.00	0.00
Si Ca Al	21.36	0.00	9.39	76.53	11.74	2.35	0.00	0.00
Si - -	5.32	0.00	0.00	33.96	52.83	11.32	1.89	0.00
Si Al -	5.22	0.00	0.00	3.85	78.85	17.31	0.00	0.00
Si Al K	15.55	0.00	0.00	1.29	80.00	16.77	1.94	0.00
Others	40.32	0.00	37.56	59.70	2.74	0.00	0.00	0.00
Totals	100.00	0.00	17.15	53.06	24.67	4.71	0.40	0.00

interact during combustion to form intermediate ash compositions. This trend is also well represented by the model results although, as for Kentucky #11, the predicted compositions are deficient in Al. The ASTM ash composition is again seen to inadequately represent the range of ash compositions. Figure 7.9-10 shows the major ash composition categories. Although the full coalescence model reproduces the experimental trends for Si and SiAl reasonable well, it overpredicts the amount of SiAlK and fails to correctly partition the Ca with the aluminosilicates. However, Figure 7.9-11 shows that the total calcium aluminosilicate ash (SiAlCa + SiCaAl) is correctly predicted, whereas the no coalescence model severely underpredicts this type. The results indicate significant interaction of illite with other minerals, but even in the full coalescence limit the potassium aluminosilicate ash content is overpredicted. The comparison of the ash psds measured at PSIT to that predicted

FIGURE 7.9-2. - Coal PSD for selected coals.

TABLE 7.9-7. - Mineral size distribution data - raw coals

Illinois #6 Raw Coal								W. Kentucky #11 Raw Coal							
Mineral	Wt % in Mineral Matter	Size Distribution in Microns						Mineral	Wt % in Mineral Matter	Size Distribution in Microns					
		<2.5	2.5→5	5→10	10→20	20→40	>40			<2.5	2.5→5	5→10	10→20	20→40	>40
Quartz	20	20	27	24	22	5	1	Quartz	19	19	25	23	16	12	5
Kaolinite	6	29	29	18	21	4	0	Kaolinite	8	33	16	28	12	6	4
Illite	10	35	29	21	11	4	0	Illite	16	34	24	21	8	9	4
Mix.Sil.	18	30	27	19	14	5	4	Mix.Sil.	23	26	14	20	15	14	11
Pyrite	28	8	6	10	33	29	13	Pyrite	24	10	9	14	14	21	33
Calcite	7	8	6	7	25	21	32	Calcite	5	1	0	4	54	41	0
All Min.	100	22	17	15	23	15	8	All Min.	100	24	15	18	13	15	16
Upper Freeport Raw Coal								San Miguel Texas Lignite							
Mineral	Wt % in Mineral Matter	Size Distribution in Microns						Mineral	Wt % in Mineral Matter	Size Distribution in Microns					
		<2.5	2.5→5	5→10	10→20	20→40	>40			<2.5	2.5→5	5→10	10→20	20→40	>40
Quartz	10	8	14	26	20	26	6	Quartz	12	15	26	23	17	14	5
Kaolinite	7	15	9	15	25	19	16	Kaolinite	2	-	-	-	-	-	-
Illite	35	10	10	13	11	12	44	Illite	16	25	12	23	20	13	6
Mix.Sil.	19	12	16	15	21	12	23	Mix.Sil.	64	7	10	15	30	27	10
Pyrite	18	4	2	13	13	14	54	Pyrite	2	-	-	-	-	-	-
All Min.	100	9	10	15	15	14	36	All Min.	100	13	12	17	26	22	9

FIGURE 7.9-3. - Mineral and ash compositions (Kentucky #11).

FIGURE 7.9-4. - Ash composition: model versus experiments (Kentucky #11).

FIGURE 7.9-5. - Ash PSDs: model versus experiments (Kentucky #11).

B-7123

FIGURE 7.9-6. - Coal PSDs: actual and fine (Kentucky #11).

B-7120

FIGURE 7.9-7. - Ash PSD: mode (fine #2) versus experiments (Kentucky #11).

FIGURE 7.9-8. - Ash PSD: model (fine #1) versus experiments (Kentucky #11).

by the full coalescence model (Figure 7.9-12) indicates limited coalescence above 15 μm . Why the full coalescence model predicts a slightly finer distribution below 15 μm is not yet understood. It may be because the coal psd for the smallest particle sizes has been either inadequately measured or that departures from a random distribution of minerals favor these sizes.

7.9.3.3 Upper Freeport

Predictions and measurements for the major ash composition categories are shown in Figure 7.9-13. Differences between the full and no coalescence limits are not large, although the experimental results indicate that coalescence of quartz and pyrite minerals does take place. This trend is found in the full coalescence results. As for Kentucky #11, the full coalescence model again significantly overpredicts the amount of iron aluminosilicate ash. All other categories are well predicted by the full coalescence model. Measured and predicted ash psds are compared in Figure 7.9-14. The full coalescence limit provides a much better representation of the distribution below 15 μm than does the no coalescence whereas above 15 μm this situation is reversed, suggesting that only limited coalescence of the larger minerals is occurring.

7.9.3.4 Illinois #6

Predicted and measured major ash categories are compared in Figure 7.9-15. The no coalescence limit fails to predict the iron and calcium aluminosilicate ash categories and overpredicts the amounts in all other categories. The full coalescence limit is generally in good agreement with the measured results although, as seen before, it overpredicts the amount of iron aluminosilicate ash. The results indicate that significant mineral coalescence

FIGURE 7.9-9. - Mineral and ash compositions (San Miguel Lignite).

FIGURE 7.9-10. - Ash composition: model versus experiments (San Miguel Lignite).

FIGURE 7.9-11. - Ash composition: model versus experiments (San Miguel Lignite).

FIGURE 7.9-12. - Ash PSDs: model versus experiments (San Miguel Lignite).

FIGURE 7.9-13. - Ash composition: model versus experiments (Upper Freeport).

FIGURE 7.9-14. - Ash PSDs: model versus experiments (Upper Freeport).

FIGURE 7.9-15. - Ash composition: model versus experiments (Illinois #6).

is occurring. This is supported by the ash psds shown in Figure 7.9-16. The particle size distribution predicted in the full coalescence limit is far superior to that of the no coalescence limit over the entire size range. However, even in the full coalescence limit the predicted psd is slightly finer than what is measured. As for San Miguel, this may indicate a problem with the measured coal psd for the smallest sizes or with its discrete representation in the model.

One can also examine the individual ash compositions in terms of a traditional index such as the base/acid ratio. Figure 7.9-17 illustrates the wide variability in the base/acid ratio found for ash particles compared to the ASTM mean value. The wide spread arises from the range of chemical compositions of the ash particles. Clearly, the mean value does not adequately represent the mass of problematic particles. Aside from a modest discrepancy near the mean value, the full coalescence model is seen to represent the measured variability reasonably well.

7.9.4 Discussion of Results

Based on the above results, the full coalescence model gives generally acceptable predictions of ash composition and size distributions. On the other hand, the no coalescence model fails to identify several ash composition categories and consistently predicts too fine an ash size distribution in the smaller size range.

FIGURE 7.9-16. - Ash PSDs: model versus experiments (Illinois #6).

FIGURE 7.9-17. - Base/acid ratio variability for Illinois #6 ash particles.

Comparing both sets of predictions with the measurements, one can conclude that quartz, pyrite, and illite undergo some coalescence. The full coalescence limit, however, predicts a much higher concentration of iron aluminosilicate ash particles for the three bituminous coals than is observed in the CCSEM analysis of the ash. In fact, the total iron concentration in the combustion ash, as determined by the CCSEM technique, is consistently lower than that found by either ASTM ash analysis or CCSEM mineral analysis (Boni et al., 1990). This inconsistency might arise from incomplete coalescence of pyrite and aluminosilicate minerals, resulting in ash particles with nonhomogeneous compositions (Helble et al., 1991). Because the no coalescence limit fails to account for mineral interactions that yield iron- and calcium aluminosilicate ash, it overestimates the concentrations of iron-rich, silicon-rich, and illite-rich ash particles. Calcium aluminosilicate ash results mainly from the interaction of organically-bound calcium with aluminosilicate minerals. Calcium, present as calcite, does not interact with other minerals, unless it is present as very fine inclusions. The compositions and concentrations of calcium-containing ash particles are sensitive to the amount of organically-bound calcium in the coal. In addition, since the calcium is not uniformly dispersed in the ash particles and tends to be segregated near the particle surface, the measured compositions are higher in calcium than the bulk average (Boni et al., 1990). Consequently, the full coalescence limit, which assumes homogeneous particles, does not correctly predict the surface concentrations as measured by the CCSEM.

Comparison of the predicted and measured ash psds establishes that full mineral coalescence is responsible for generation of ash particles smaller than 15 μm . For larger ash

particles, the results suggest that limited coalescence occurs for all coals except Illinois #6. Limited mineral coalescence can be due to either char fragmentation prior to coalescence or coalescence times longer than the char burning times. Fragmentation of the char is favored in particles that form cenospheres, for which the thin shell burns out before the minerals around the periphery come into contact. Long coalescence times are needed for highly viscous particles and occur at lower combustion temperatures and for larger mineral inclusions.

Additional factors that need to be considered to improve predicted ash composition and size distributions include char and mineral fragmentation, nonrandom mineral associations in coal particles, incomplete coalescence resulting in agglomerates with highly nonuniform compositions, vaporization of small inclusions and organically-bound sodium and potassium, and the condensation of the resulting vapor species on small ash particles altering their surface composition. Moreover, all current mineral redistribution models fail to exclude the proper fraction of small minerals. Since minerals are excluded only if they do not fit in a coal particle, no small minerals are now excluded. This is inconsistent with observations of fine excluded minerals in coal samples. Recent advances in CCSEM capability afford the possibility of distinguishing between included and extraneous minerals (see, for example, results in Section 7.6 of this report). This will result in greatly improved predictions of minerals included in coal particles.

7.9.5 Char Fragmentation Modeling

In this subsection, the development of an algorithm for treating the effects of char fragmentation on ash particle release during char particle burnout is discussed. This initial effort was devoted to ash formation from the bituminous coals, Illinois #6, Kentucky #9 and 11, and Upper Freeport. Because these coals have moderate to high tendencies to form cenospheres, our attention centered on calculating ash release from cenospheric char particles. However, in a certain limit, the algorithm developed is also applicable to non-cenospheric char particles. The approach that we have taken is a direct outgrowth of many of the ideas developed at MIT by Kang (1991) in his Ph.D thesis. In the following sections we describe the basic ideas underlying the computation of the number and sizes of ash particles released from the char particle. Then we indicate in general terms how the ash release algorithm operates in the present mineral redistribution code. Finally, results are presented for Illinois #6.

7.9.5.1 Ash Release from Cenospheric Char Particles

During the pyrolysis and devolatilization of pulverized bituminous coal, many particles become plastic and deform into thin-walled cenospheres due to high internal gas pressure. We will assume that most of the initial mineral content of each coal particle is retained in or on the cenosphere shell. During the subsequent burnout of the cenospheric char particle, the shell becomes thinner and weaker. Any large pores (blowholes) in the shell will lead to lateral burning of the shell and further weaken it. As the char matrix shrinks, mineral inclusions trapped in it are brought into contact. If the inclusions are

molten, they may then coalesce. Eventually, the shell either burns out fully or breaks into a number of fragments. Either way, the coalesced mineral inclusions are released, producing ash particles whose size and composition are determined by the mineral particles found within localized sections of the shell or in the shell fragments.

The present mineral redistribution code provides us with a discrete set of coal particles of known mineral content giving us the capability of generating ash particles from each coal particle. In order to determine the number and size of the mineral inclusions that coalesce during burnout we adapt the ideas of Kang (1991) whose approach was analogous to that used to treat molecular collisions in the kinetic theory of gases. The basic idea is that as the cenosphere shell burns and becomes thinner, mineral inclusions at the edges of the shell are brought into contact with other inclusions that become exposed as the char burns away. If we assume that all such contacts result in coalescence, we need only estimate the number of such "collisions" that occurs for each mineral particle in order to calculate the final size of the ash particle released.

The number of mineral particles of diameter D_j contacted by a larger mineral particle of diameter D_i can be estimated by computing the volume encompassed by these two particles as the shell burns out and multiplying this volume by the number density of minerals of size j in the shell. As sketched in Figure 7.9-18, this volume is proportional to the effective "collision cross-section" of the two particles times the thickness of the cenosphere. The volume of particle i should also be subtracted from the volume swept out because the "collision partners" (the size j particles) are excluded from char occupied by the size i particle. Similarly, in computing the number density of mineral particles of a given size in the cenosphere, the shell volume should be corrected for the volume of all larger mineral particles. Mineral particles are obviously excluded from shell volume occupied by

FIGURE 7.9-18. - Two-dimensional schematic of interaction region swept out by mineral particles of diameter D_i and D_j during burnout. Only particles whose centers lie within the circular cross section of diameter $D_i + D_j$ will be intercepted by the larger mineral particle.

the larger minerals, effectively increasing their number density in the remaining carbon matrix. Thus the number of size j particles encountered by a size i particle, N_{ij} , is simply

$$N_{ij} = V_{ij}\rho_j, \quad (7.9-1)$$

where, assuming spherical mineral particles, the encounter volume V_{ij} is given by

$$V_{ij} = \pi(D_i + D_j)^2\delta_e/4 - \pi D_i^3/6, \quad (7.9-2)$$

and δ_e is an effective length discussed below. The number density ρ_j of size j particles is

$$\rho_j = n_j/V_j^s, \quad (7.9.3)$$

where n_j is the number of size j mineral particles in the shell, and the effective shell volume, V_j^s , for these particles is

$$V_j^s = (\pi/6)[(D_O^3 - D_I^3) - \sum_{i>j} D_i^3]. \quad (7.9-4)$$

In these equations, D_O and D_I are the outer and inner diameters, respectively, of the cenospheric particle. The effective length, δ_e , in Eq. (7.9-2) is related to δ , the thickness of the cenosphere shell,

$$\delta = (D_O - D_I)/2, \quad (7.9-5)$$

but its specific value depends on two principal considerations. First, δ_e should reflect the radial dimension of the shell volume containing all the mineral particles destined to end up as a single ash particle. Clearly, δ is an upper bound for this value. A smaller value is possible if the shell contained a sizeable fraction of pores large enough to disengage any ash particle encountering such a pore. Kang (1991) has shown that the separation length can be estimated from the formula

$$L_s = (2/3)D_p(1-\phi_p)/\phi_p, \quad (7.9-6)$$

where D_p is the diameter of the pore encountered by the ash particle and ϕ_p is the porosity associated with those pores. Obviously, in most situations, D_p must exceed the ash particle diameter in order for the ash particle to be released. As discussed later, δ is typically 10 to 30% of D_O , that is, between 1 and 3 μm for the smallest coal particles and between 20 and 60 μm for the largest. Mineral particles larger than δ will not undergo coalescence for geometric reasons unless they are captured within the cenosphere interior - a special case. Purely geometric considerations imply that for mineral particles occupying a substantial fraction of the shell thickness, for example those with $D_i > \delta/3$, it is unlikely that large pores with $D_p > D_i$ will be found between the mineral particle and the shell boundaries often enough to effect significant ash release. Thus, for this case we must have $L_s \approx \delta$. In larger

FIGURE 7.9-19. - Two-dimensional illustration of conical volume swept out by two mineral particles due to spherical shape of char particle.

coal particles, smaller mineral particles will be captured efficiently by larger mineral particles precluding their release by intercepting a smaller pore. Again, we have $L_s \approx \delta$. Finally, if we consider small mineral particles ($D = 2.5 \mu\text{m}$) in small coal particles ($D_O = 10$ to $20 \mu\text{m}$), we find from Eq. (7.9-6) (with $D_p = 2.5 \mu\text{m}$ and $\phi_p = 0.2$) that $L_s = 6.7 \mu\text{m}$, a value larger or, at best, comparable to δ . Thus we conclude that δ is a suitable initial estimate for the separation length. A second consideration addressed by Kang (1991) concerns the effect of the geometry of the spherical shell on the coalescence process. As burning proceeds, particles initially too far apart to coalesce in a linear burning geometry can approach each other as the spherical particle shrinks. Thus additional volume is consumed bringing more mineral particles together. The situation is illustrated in Figure 7.9-19. Kang (1991) estimated a conical correction factor for this effect by taking the shell volume times

the ratio of the mineral particle cross-sectional area to the total area of the spherical surface at the inner ash separation distance. In this case, that corresponds to the inner surface of the cenosphere. Thus we find

$$\pi(D_i + D_j)^2 \delta_e / 4 = (\pi/6)(D_O^3 - D_I^3) \pi(D_i + D_j)^2 / (4\pi D_I^2) . \quad (7.9-7)$$

Upon simplifying, we obtain

$$\delta_e = (\delta/3)(1 + \gamma^{-1} + \gamma^{-2}) , \quad (7.9-8)$$

where

$$\gamma = D_I / D_O . \quad (7.9-9)$$

From Eqs. (7.9-8) and (7.9-9), we see that in the limit of very thin shells (i.e., $\gamma = 1$), $\delta_e = \delta$, but that for thicker shells the conical correction factor can become significant.

We next address the calculation of δ , the shell thickness. The following considerations based on conserving volume lead to apparently reasonable estimates. Let V be the initial total volume of the coal particle and V_M be the volume of its included mineral matter. Then the initial "carbon" volume is simply $V - V_M$. If f_v is the volatile carbon fraction and ϕ is the total porosity of the shell after swelling and devolatilization, then the total volume of the shell is $(V - V_M)(1 - f_v)/(1 - \phi) + V_M$. In terms of D_I and D_O , we have

$$(\pi/6)(D_O^3 - D_I^3) = (V - V_M)(1 - f_v)/(1 - \phi) + V_M . \quad (7.9-10)$$

To account for the possibility of swelling, we introduce an empirical swelling index S , such that

$$(\pi/6)D_O^3 = SV. \quad (7.9-11)$$

Upon combining Eqs. (7.9-10) and (7.9-11) and solving for D_I/D_O , we find

$$\gamma = D_I/D_O = \{1 - S^{-1}[(1 - V_M/V)(1 - f_v)/(1 - \phi) + V_M/V]\}^{1/3}. \quad (7.9-12)$$

Finally, Eqs. (7.9-5) and (7.9-9) enable us to express δ in terms of γ :

$$\delta = D_O(1 - \gamma)/2. \quad (7.9-13)$$

For coal particles large enough to representatively sample the entire mineral size distribution, V_M/V and, hence γ , will be independent of coal particle size. To make a simple estimate of δ , let $V_M/V = 0.1$, $f_v = 0.4$, $\phi = 0.2$, and $S = 1$. We then find $\gamma = 0.61$ and $\delta = 0.2D_O$, which seems reasonable.

We conclude this description of ash release by considering one other possible ash coalescence mechanism. If the cenospheric shell contains one or more large blowholes, the transport of oxygen into the particle interior will not be hindered, and burning of the interior shell surface is likely to proceed at a rate comparable to that of the external surface. In this case, ash particles will be formed on the inner side of the shell where, due to their spatial confinement, they have a high probability of coalescing with each other to form a larger, "interior" ash particle. To estimate the fraction of ash particles that may coalesce in this way, we imagine that the inner and outer shell surfaces have the same linear recession rate, and we compute the fraction of shell volume consumed by interior burning. The two fronts meet halfway through the shell (an excellent approximation for $D_O = D_I$, i.e., thin walled cenospheres). Thus the fraction x_c of mineral particles coalescing to form the interior ash particle is given by the volume ratio,

$$x_c = [(D_O - \delta)^3 - (D_O - 2\delta)^3] / [D_O^3 - (D_O - 2\delta)^3]. \quad (7.9-14)$$

With Eq. (7.9-13) this expression can be simplified to read

$$x_c = [(1 + \gamma)^3/8 - \gamma^3] / (1 - \gamma^3). \quad (7.9-15)$$

With the above estimate of $\gamma = 0.61$, we find $x_c = 0.38$. Thus for situations in which this interior ash coalescence mechanism can occur, we expect a significant reduction in the number of ash particles released per coal particle.

To get a rough idea of the number and size dependence of the ash particles released as a function of coal particle size, we adapt another argument of Kang (1991). To simplify matters we assume that all mineral particles are the same size. Kang argued that the number of mineral particles coalescing to form a single ash particle could be estimated as the ratio of

the separation length L_s and a coalescence length L_c . We have already suggested that for cenospheric ash release $L_s \approx \delta$. From the mineral particle number density ρ , we may estimate that $L_c \approx (\rho)^{-1/3}$. Thus the number N_{af} of ash particles/char fragments may be obtained by dividing the number of mineral particles per coal particle by the number of mineral particles per ash particle. We find

$$N_{af} \propto (\rho \delta D_O^2) / (\delta / (\rho)^{-1/3}) , \quad (7.9-16)$$

which simplifies to

$$N_{af} \propto D_O^2 \rho^{2/3} . \quad (7.9-17)$$

Since ρ is independent of D_O , at least for larger coal particles, we see that N_{af} is predicted to vary as the square of the coal particle diameter for this model of cenospheric ash release. The average fragment size V_f is also predicted to increase linearly with coal particle diameter,

$$V_f \propto (\delta D_O^2) / N_{af} = \delta / \rho^{2/3} , \quad (7.9-18)$$

since δ varies linearly with D_O as seen in Eq. (7.9-13).

7.9.5.2 Description of Ash Release Algorithm

To implement the above description of ash release in the engineering model computer code, the following procedure is used. The initial stages of the calculation are carried out using the mineral redistribution code described in previous quarterly reports and a conference paper (Wilemski et al., 1991). After the mineral inventory of each coal particle is established, the ash release procedure is begun. In the present version of the code, to simplify the bookkeeping involved, coal particles are analyzed in order of largest to smallest, followed by the analysis of all excluded mineral particles. To compute the ash released from a given coal particle, the code first calculates δ and D_O via Eqs. (7.9-11) through (7.9-13). Next the number densities ρ_i of the different sized mineral particles are computed from Eqs. (7.9-3) and (7.9-4). The final preliminary step involves Eqs. (7.9-1) and (7.9-2) to calculate the N_{ij} factors, the average numbers of various sized mineral particles that coalesce into a single ash particle.

The next step determines the fate of all mineral particles whose diameter exceeds δ . The fraction x_c of these particles is retained as part of the interior ash particle, if that option is in force. The remainder are placed into the excluded mineral category on the grounds that they would be released from the char during burnout with little or no coalescence with smaller particles. After this step only minerals smaller than δ are left in the shell. Of these the fraction x_c of each size and type is randomly selected for inclusion in the interior ash particle, if one is being formed. The remaining particles are then combined to form ash particles in a sequential process beginning with the largest mineral particles, since these occupy the largest volume of char.

The mineral particles of each size to be combined with a given particle are selected randomly (averages are used if the numbers are large), and the inventory of mineral sizes and types is adjusted at each step. After the smallest mineral particles have been added, organically bound inorganics are added in proportion to the char volume "consumed" in forming this ash particle. The ash particle is then analyzed, as in the earlier code, to determine its size and composition, and the results are stored to await statistical analysis after all ash particles have been treated. When particles of a given size are exhausted in the shell, mineral particles of the next smaller size are then considered as the seed particles for the accumulation of the remaining smaller mineral particles. In this way, a sequence of ash particles of descending size is generated from each coal particle. Figure 7.9-20 schematically illustrates the ash generation procedure from a cenospheric char particle.

FIGURE 7.9-20. - Schematic representation of ash particle formation and release from a cenospheric char particle. Minerals within the dashed sectors come into contact and coalesce during burnout. Only four ash particles are shown, although many hundreds are typically produced from the larger coal particles.

The algorithm outlined above has been fully coded (with one exception noted below) and debugged. The code runs successfully and appears to give satisfactory results in qualitative accord with our intuitive expectations. However, much testing and refinement of the algorithm remains to be done. In addition, the treatment of ash release from the $10\text{ }\mu\text{m}$ coal particles is presently incomplete. Because they are much more numerous than any other size range, these particles are stored as several hundred classes of the most probable types rather than individually. The current treatment of the $10\text{ }\mu\text{m}$ coal particles results in every particle of each class being treated identically, whereas some allowance should be made for the statistical variations that are bound to occur. The net effect on the results is that there is some uncertainty regarding the ash particle distribution in the smallest two ash size classes. A further complication stems from the simulation of ash formation using a small number (6) of discrete mineral sizes. As a consequence, the resulting ash particles are distributed over discrete sizes that are a particularly poor representation of a continuous size spectrum at the small end, i.e., for ash diameters $< 20\text{ }\mu\text{m}$. Various strategies for accurately simulating a continuous size spectrum are being considered.

An example of the results produced by the current version of the model is shown in Tables 7.9-8 and 7.9-9 for Illinois #6. The full ash release procedure, as described above, was used to generate these results, which should be considered merely as indicative of the capabilities of the model and not as an ultimate prediction to be compared with experiment. Nevertheless, the total number percents listed in Table 7.9-8 agree reasonably well with the measured values, which are listed for comparison, except for the 10 to 20 μm particles. The discrepancies could easily be due to the generation of discrete ash sizes mentioned above, although more work is needed to confirm this. Table 7.9-9 provides a detailed breakdown of the numbers and sizes of ash particles produced by each coal particle size class. The first two columns list, respectively, the number of coal particles initially generated in each size class and the number analyzed for ash release. The discrepancy in the 10 μm class is due to the presence of small coal particles without any included mineral particles. Mineral particles that are reclassified as excluded during the ash release procedure are also not counted as ash particles produced from a class of coal particles. This accounts for the further reduction in the number of ash particles produced by 10 μm coal particles that is evident in column 3. Results of this type will assist us in ascertaining whether the char fragmentation model presented herein is correctly simulating the key physical features responsible for ash coalescence and release during burnout.

7.9.6 Conclusions and Significance

Traditional indices for slagging and fouling based on mean ASTM ash compositions are inadequate because they fail to account for the wide variability in compositions and sizes of ash particles. The analysis of coal using CCSEM provides detailed information regarding the sizes, types and abundance of the various minerals present in the coal. The availability of this information is stimulating rapid development of theoretical models for predicting distributions of ash composition and size. One promising class of models is based on the redistribution of minerals among coal particles to simulate the particle-to-particle variability of mineral content found in pulverized coal. The resulting ensemble of coal particles with included and extraneous mineral can be converted into an ash distribution by using realistic simulations of the important physical and chemical transformations and interactions of the minerals. Even the simple full coalescence limit for the included minerals provides a reasonable measure of the variability of ash composition and size. Size information is needed to determine rates of ash transport to heat transfer surfaces. Composition data are needed to ascertain ash stickiness, deposit growth and heat transfer rates, and soot-blower performance. Detailed flyash size and composition data will also be useful for predicting electrostatic precipitator performance.

7.10 Phase II Conclusions - Tasks 7 and 8

In this section, significant conclusions derived from the Phase 2 effort at PSI Technology Co. are briefly summarized. Detailed conclusions for individual subtasks were described in detail in the individual subsections (7.3 through 7.9) of this report; the reader is referred to these sections for additional discussion.

TABLE 7.9-8. - Size distribution for each fly ash type (number % in each fly ash type) for Illinois #6 coal

Minerals	% of Total	Size Range (μm)						
		0.0-2.5	2.5-5	5-10	10-20	20-40	40-80	80-500
Si	13.98	56.25	23.66	17.86	2.10	0.12	0.00	0.00
Si Al K	47.90	71.76	20.00	7.41	0.78	0.04	0.00	0.00
Si Fe Al	14.51	11.81	87.05	0.52	0.47	0.15	0.01	0.00
Si Al	11.31	76.07	15.74	7.31	0.82	0.07	0.00	0.00
Si Fe Al	2.06	0.00	75.20	23.12	1.31	0.36	0.01	0.00
Fe	6.09	86.62	7.00	4.71	1.40	0.27	0.01	0.00
Ca	1.22	74.87	13.68	8.41	2.52	0.46	0.06	0.00
Si Al Ca	2.35	0.00	94.67	3.91	1.37	0.06	0.00	0.00
Others	0.57	0.00	62.69	23.17	10.87	3.17	0.10	0.00
Totals	100.00	58.75	32.03	8.04	1.06	0.11	0.00	0.00
Measured		47.1	32.9	10.9	8.1	0.9	0.1	0.0

TABLE 7.9-9. - Coal particle number distribution and number of ash particles produced for Illinois #6 coal

Avg. Size (microns)	Input	Output		Ash Number Distribution for Each Coal Size Range (µm)								
	# Coal	# Coal	# Ash	Avg #/Coal	0-2.5	2.5-5	5-10	10-20	20-40	40-80	80-500	
Excluded	114595	114595	114595	1.0	82215	25300	5509	1384	173	14	0	
10.00	154984	113499	78268	0.7	0	77383	885	0	0	0	0	
20.00	26713	26713	185467	6.9	132517	41898	9632	1420	0	0	0	
30.00	5241	5241	110879	21.2	90132	8084	11792	805	66	0	0	
40.00	1850	1850	68723	37.1	45268	14623	8044	667	121	0	0	
50.00	639	639	42422	66.4	25618	10578	5553	586	87	0	0	
60.00	285	285	30002	105.3	15482	9125	4411	899	84	1	0	
70.00	146	146	21654	148.3	9568	8446	3010	585	44	1	0	
80.00	60	60	12172	202.9	4213	5812	1807	285	54	1	0	
90.00	32	32	8407	262.7	1997	4893	1303	182	30	2	0	
100.00	19	19	6118	322.0	670	4247	1035	147	18	1	0	
110.00	12	12	4567	380.6	5	3606	797	122	37	0	0	
120.00	7	7	3232	461.7	5	2531	583	85	28	0	0	
130.00	2	2	1085	542.5	1	844	199	34	7	0	0	
140.00	4	4	2536	634.0	3	1955	488	71	15	4	0	
150.00	3	3	2254	751.3	2	1740	438	59	12	3	0	
160.00	2	2	1599	799.5	0	1219	317	51	10	2	0	

7.10.1 Chemical Composition Distributions of Ash Particles

One of the most important results from this program was the characterization of the fly ash particle composition distributions. For all coals examined, including the < 1% ash content chemically cleaned coals, a broad distribution of ash particle compositions was obtained. This finding clearly indicates that the assumption of a single "mean" size and "mean" composition is a poor representation of combustion-derived ash.

The beneficiated Illinois #6 SOAP and the blended coal demonstrated the mineral interactions that would have been expected, given the composition of the parent coals. Differences appeared to be related to the amount of a given mineral remaining in the fuel; no significant changes in interacting minerals were identified. For the chemically cleaned Gravimelt coals, however, the removal of most of the major mineral species led to the formation of some titanium aluminosilicates not observed elsewhere. This suggested the presence of fine grained or organically associated titanium that was not removed by cleaning.

7.10.2 Effects of Combustion Scale

In both phases of this program, experiments with identical coals were conducted at MIT, PSIT, and UA. Each facility, however, has experimental reactors of different scale. At PSI Technology Co., a laminar flow isothermal drop tube furnace was used, with a methane/air burner that preheats the gases preceding the electrically heated portion. Facilities at MIT and UA were an order of magnitude smaller and larger, respectively, in coal feed capacity.

With these facilities and the use of identical coal samples, the effects of combustion scale could be directly examined. It was found that ash particle size and chemical composition distributions agreed well if combustion conditions were comparable at the three facilities. That is, if coal particle combustion temperatures were comparable at PSIT and UA, particle size distributions were found to be in good agreement with one another (comparison with MIT results was not made because of the differences in coal psds). Within narrow bounds (i.e., 7% to 21% oxygen, or stoichiometric ratios of approximately 1.5 to 4.5), little change was noted in the size or composition of the ash for the four coals examined under these conditions. Examination of the composition distribution at the three facilities revealed that similar ash phases were formed in all. It was observed, however, that the amount and composition of the submicron ash fume was much more sensitive to differences in combustion conditions, coal particle size distribution, and temperature history. The amount of fume generated at MIT in the dilute experiments was routinely the highest, and increased significantly with increasing oxygen partial pressure. PSIT and UA facilities showed comparable lower levels.

From this analysis, it was concluded that *coal mineralogy* and combustion temperature are the most important parameters determining the composition distribution of combustion-derived fly ash particles.

7.10.3 Effect of Reducing Conditions

Limited Phase II experimentation was conducted to explore the impact of reducing conditions on ash formation. In a series of experiments with Phase II Eagle Butte and Kentucky #9 coals, gas temperature was held constant at 1650 K while the stoichiometric ratio was varied from 0.9 to 3.4. Examination of the ash by CCSEM revealed that for each coal, changing stoichiometry had little effect on the particle chemical composition distributions. In all cases, however, the amount of submicron fume increased with increasing oxygen level, a result of the increase in particle combustion temperature with increasing O_2 . These results suggest that conditions more severely reducing than $SR = 0.9$ may be required to affect coalescence and fly ash particle composition.

7.10.4 Pilot Scale Testing at SECV

Under an IEA Annex I Agreement, PSIT collaborated with the State Electricity Commission of Victoria (SECV) in pilot scale tests of three low-rank coals. Beulah lignite, Loy Yang 1953, and a chemically treated sample of LY 1953 were studied in the SECV 1,000,000 Btu/h (0.3 MW_{th}) combustor. Loy Yang and treated Loy Yang tests were designed to assess deposition and deposit control, whereas Beulah tests were designed to assess ash formation for comparison with earlier program results. The Beulah lignite coal was provided in crushed form by this program; thus, it was identical in mineral and ash *content* to the coals examined at PSIT, UA, and MIT. Coal and mineral size distributions differed from those tested at the other facilities, however, because of the difference in pulverizers used. Direct size comparisons among facilities were therefore not expected to be conclusive; ash particle composition comparison could, however, be made if no significant differences in mineral distribution resulted from the differences in pulverization. These tests therefore provided an opportunity to further assess the mechanisms of ash particle formation and deposition, and determine again whether combustion scale (and the associated temperature profile) affected our conclusions.

Ash particle samples were collected isokinetically from the combustion chamber, from the horizontal duct upstream of the deposition test banks (i.e. convective section), and from the electrostatic precipitator hoppers. Examination of Beulah lignite ash samples revealed nepheline-like sodium aluminosilicate compositions similar to those observed in PSIT and UA testing of this coal. Calcium aluminosilicate compositions similar to those observed during Beulah testing at PSIT and UA were also observed. Calcium sulfate-sodium sulfate solid solutions, identified previously in smaller ash particles collected in UA tests, were also seen in the smaller ash particles here.

These results provide confirmation of the conclusion drawn from a prior comparison of PSIT/UA results, and examination of the effects of variable stoichiometry. In all systems examined, from 0.15 kW_{th} to 0.3 MW_{th}, using a common Beulah lignite coal, that ash particle composition distribution was insensitive to combustion scale. Specific mineral interactions were therefore common to all facilities for the coal examined.

7.10.5 Clay Mineral Transformations

The transformations of excluded kaolinite, montmorillonite, and nepheline were also examined in a drop-tube furnace study. Neither melting nor gas evolution were evident for either of two kaolinite samples subjected to temperatures of 1650 K. For the excluded montmorillonite, rapid melting resulting in smooth, glassy spheres that were sticky upon impact with deposition surfaces. For the excluded nepheline, which had a considerable potassium-rich aluminosilicate component, neither gas evolution nor melting were observed at gas temperatures up to 1650 K. These results suggest that montmorillonite ash may contribute significantly to deposit initiation, whereas kaolinite and nepheline may not.

7.10.6 Stickiness of Ash From Beneficiated Coals

In Phase 1, the viscosity of individual ash particles was shown to be the important parameter in determining the stickiness of ash particles upon impact with a clean high temperature tube surface. In experiments conducted in a drop tube furnace, deposition experiments conducted with the coals from Phases I and II demonstrated a wide range of ash particle stickiness behavior. For the Phase I coals, the stickiness of the coal ashes at similar impaction conditions and identical temperature was found to be San Miguel > Beulah, Eagle Butte > Kentucky #11 > Kentucky #9, Upper Freeport, Illinois #6 > Loy Yang. Calcium-rich aluminosilicate ash particles appeared to be the most likely to initiate deposition. Note that this ranking is for collection efficiency - the impaction efficiency or size distribution of the ash particles is not included. The stickiness of all four of the low-ash Phase II coals (Gravimelt 7A, Gravimelt 9C, Illinois #6 SOAP, Loy Yang 1953) was significantly lower than any of the Phase I U.S. coals at comparable conditions. Only the Loy Yang 2301 produced collection efficiencies as low as the Phase II coals (typically < 10% of the ash at approximately 1500 K). Although low impaction efficiencies do contribute to the apparent lower values for Phase II coals, the lack of significant calcium aluminosilicate formation tended to keep absolute stickiness at a low value as well. Thus, ash from these coals was less likely to impact, and less likely to stick upon impaction than ash from "raw" coals.

Deposition tests utilizing Beulah lignite, Loy Yang 1953, and treated Loy Yang 1953 coals were also conducted at the pilot scale facilities at SECV. For the Beulah lignite, short term uncooled probe samples showed iron enrichment in the deposit initial layers, suggesting deposition of molten pyrite-derived species. Longer term and lower temperature deposition probe samples showed a doubling of the Ca/Fe ratio, suggesting calcium aluminosilicate deposition was more important at later times. Compared to Beulah lignite, much smaller deposits were observed during testing of the Loy Yang coal, due to both the lower ash content, smaller ash particle size, and reduced stickiness of the ash particles. Deposits collected from uncooled surfaces were a mixture of iron and silicon phases, suggesting possible silicate deposition. Samples collected from cooled surfaces were sodium sulfate enriched. Addition of aluminum and magnesium additives significantly reduced the amount of deposition for the Loy Yang.

7.10.7 Trace Metal Transformations

Illinois #6 and Illinois #6 SOAP coals and their combustion-derived ashes were analyzed in an initial effort to assess the effects of beneficiation on trace element transformations. Coal cleaning significantly reduced the levels of Co and Zn, slightly reduced the levels of As and Se, and had no effect on the levels of Cr and Sb. As, Sb, Zn, and Se were all enriched in the submicron ash for these coals, suggesting at least partial vaporization and recondensation.

Chromium was further analyzed by XAFS spectroscopy to identify the form of this element in the coals and ashes. Several standard materials were also examined. Results indicated that chromium was present exclusively in the less toxic +3 oxidation state. No evidence for the existence of the toxic and carcinogenic +6 form of chromium was found.

7.10.8 Engineering Model to Predict Ash Particle Size and Composition Distributions

A major "deliverable" of this project was the development of a model capable of describing the *distribution* of ash particle sizes and chemical compositions resulting from the combustion of pulverized coal. This model was developed during Phase II of this program by synthesizing the mineral redistribution model, conclusions and scaling laws derived from the char fragmentation models, and scaling laws and descriptions of mineral coalescence derived from the fundamental experiments conducted in this program.

The Engineering Model (EM) first simulates the distribution of minerals in pulverized coal by distributing them with a streamlined version of the mineral redistribution model. A composite Monte-Carlo/Poisson method was developed to minimize the computational effort required to distribute the various minerals among the wide range of coal particle sizes. This method requires less computer memory and shorter run times while handling a wider range of coal and mineral sizes than a pure Monte Carlo approach. In the composite method, the larger ($> 2 \mu\text{m}$), less numerous, mineral particles are distributed among the larger ($> 10 \mu\text{m}$) coal particles using a pure Monte Carlo method; randomly selected minerals are placed one-at-a-time into randomly chosen coal particles. An average number of 2 μm inclusions is then assigned to each large coal particle based on the mineral free volume of the particle. The redistribution of mineral particles among the smallest (10 μm) coal particles is handled using Poisson distributions. Individual coal particles are not considered. Instead, classes of small coal particles are generated to represent the most probable distributions of 2, 4, and 8 μm minerals as determined by Poisson statistics.

In addition to modeling the initial ensemble of coal and minerals, combustion transformations (mineral coalescence and char fragmentation) were also modeled to predict ash formation. Depending upon the initial distribution of minerals within coal, either full coalescence, partial coalescence, or no coalescence scenarios could be evaluated. Coalescence is governed by the mineral particle encounter probabilities determined using arguments drawn from the kinetic theory of gases. Coalescence of organically associated species such as calcium can also be included, by "defining" one of the mineral types to be

calcium. Char fragmentation, defined as an interruption to mineral coalescence, takes into account cenosphere formation and the coalescence of different sized mineral particles as the char particle shrinks during combustion.

A range of Phase I coals was examined to provide a comprehensive description of ash formation during pulverized coal combustion. For the limiting case of full coalescence, ash particle size distributions were in good agreement with experimental data. More importantly, the ash particle *composition* distributions were in good agreement with experimental data, demonstrating the ability of the model to predict information critical to the prediction of deposition, that is, the size-resolved chemical composition of individual ash particles.

7.11 Section 7 References

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