Fundamental studies of the mechanisms of slag deposit formation: Final report

Austin, L.G.; Benson, S.; Rabinovich, A.; Tangsathitkulchai, M.; Schobert H.H.

Jul 1987

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REPORTING PERIOD: Final Report

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July 1987

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INTRODUCTION

The predominant mode of combustion in utility boilers is pulverized coal firing. Pulverized coal fired boilers are generally designed for volumetric heat release rates which give a high temperature to the steam entering the turbine and hence a high generation efficiency. The behavior of inorganic constituents during combustion is one of the most important aspects that influence efficient utility boiler operation. The inorganic constituents associated with coal are converted to ash and vapor phase species during combustion and can form deposits in the boiler. This problem is aggravated by the high temperatures (1500 - 1650°C) of the pulverized coal flame. Deposition can occur on both the radiative and convective portions of the boiler. The removal of such deposits requires significant capital investments in on-line removal devices.

As a consequence of ash deposition, the heat transfer from the flame to the surfaces transferring heat to water or steam is reduced, resulting in lower steam production and causing a derating of the boiler. Problem coals cause rapid ash deposition and can eventually lead to an unscheduled shutdown of a boiler. The steel heat transfer tubes can also be damaged by corrosive constituents in the ash or vapors. Large deposits in the upper furnace area can break away from the wall tubes under their own weight, fall the considerable distance from the roof to the floor, and as a result damage tubes in the bottom of the boiler.

The loss of boiler efficiency, availability, and the cost of operational problems show that the need for additional scientific investigation on the ash deposit formation process is readily justified. The understanding of the ash deposition process has become more important as the capacity of power plants grows and new low-grade coals containing high ash contents are introduced to meet increasing energy demands.

The process of ash deposit formation is very complicated and complex. A complete understanding of this process requires knowledge of chemical composition and distribution of inorganic constituents in coal, transformations and reactions of the inorganic constituents in the flame, ash transport mechanisms, initial adhesion of ash particles to heat transfer surfaces and subsequently to each other to form a deposit, and further interactions of the deposited ash to grow a strong deposit. The interactions of deposited ash that cause changes in physical and chemical properties in an aged deposit are due to processes such as sintering, chemical reactions, and melting. The degree of these changes increases as the deposit grows from the heat transfer surfaces where it forms. All of these physical and chemical changes during the deposit formation process are not only coal-specific but also are strongly dependent on the boiler configuration and operating conditions. As a consequence, a precise and quantitative knowledge of the ash deposit formation mechanism has not yet been obtained.

The sintered strength of the ash deposit ultimately determines whether or not the accumulation can be removed from the boiler tubes by the sootblowers. If the ash particles do not sinter strongly in the deposit, they are easily blown off by the sootblowing operation. When particles sinter strongly, however, such deposits may be so resistant to fracture that normal sootblowing operations will not remove the accumulated ash from these surfaces.

The process of ash sintering to form a strong deposit mass, which follows the deposit initiation and formation, is also very complex. Fly ash is a heterogeneous material and the sintering process is often accompanied or preceded by one or more specific chemical reactions involving certain inorganic constituents in a particular ash particle. Within the ash deposit, the process of sintering and chemical reactions proceed at different rates at different locations depending on the local time-temperature history. In addition, there are many factors such as ash particle shape, particle size and distribution of sizes, furnace temperature, and atmosphere that influence the course of an ash sintering process. These factors complicate the determination of the mechanisms of ash sintering, and as a result, there is not yet sufficient information to understand the mechanisms responsible for the ash sintering involved in the deposit formation process.

The formation of tenacious deposits during the combustion of

Western coals appears to be directly related to the formation of low melting point alkali and alkaline earth aluminosilicates. Many Western coals contain significant quantities of sodium, which will volatilize during combustion, become dispersed throughout the gas stream, and later condense on other ash particles and on metal surfaces. Some sodium compounds in coal ash related systems melt at relatively low temperatures (approximately 900°C). The primary thrust of most of the past research on deposit formation from the combustion of Western coals has concentrated on the formation of melilite type crystalline phases and sodium content of the coal ash. It has been proposed that the sodium-containing material, possibly melilite, provides a binding matrix to fuse ash particles together. The mechanism of formation of melilite may be the key to understanding the depositional processes of Western low-rank coals.

All of the present empirical indices used to predict the melting and deposit-forming behavior of inorganic constituents during combustion are based on bulk ash analysis. The methods work to a limited degree but are always suspect when dealing with an unfamiliar coal because of the wide variations in ash-forming species. Hence, there exists a need for a better fundamental understanding of the formation of deposits by means of closely controlled laboratory-scale experiments and application of theoretical considerations to predict ash melting behavior.

THE DROP-TUBE FURNACE

Most of the data presented in the major sections of this report which follow were obtained using an externally heated, down-fired laminar flow furnace. These devices are familiarly known as drop-tube furnaces. Although other equipment was also used in the work reported here, the central importance of the drop-tube furnaces is such that their design and operating characteristics merit full discussion first, before the data and results obtained from them are presented.

Gas-fired Furnace

This study used vertical, externally heated tube furnaces which burned coal passed in a thin stream down the tube. The tube was heated to simulate the time - temperature history of a pulverized coal flame in a utility boiler. The gas-fired furnace was designed to maintain a combustion zone temperature of up to 1750°C inside the muffle tube to simulate the flame zone of a boiler, with exit gas temperatures between 1000 and 1300°. The length of the furnace, diameter of the muffle tube, coal feed rate, and air flow rates were all dictated by particle residence time, which was selected to be between 1 and 2 seconds under laminar flow conditions. In addition, an air/fuel ratio giving 20% excess air was essential to simulate the combustion

conditions of a utility boiler. A pulverized coal feed was used in the tube furnace, giving micrometer-sized ash particles. The fly ash formed was accelerated and then impacted on an oxidized steel substrate held at a temperature comparable to that of a waterwall tube surface.

The general arrangement of the test system is shown in Figures 1 through 5. The muffle furnace tube, made of 99.8% fused alumina, is 6.35 cm internal diameter x 90 cm long. It has a zone of maximum temperature about 50 cm long. It is heated by three tangentially fired natural gas - air burners; the temperature is controlled by adjusting the air/fuel ratio. In general, gas temperatures along the centerline of the furnace tube are about 30° C lower than wall temperatures at the same position within the furnace hot zone.

The coal feed system originally used a fluidized bed feeder which entrains pulverized coal in the primary air stream (about 1 liter/min). The feeder assembly rests on a balance to monitor the coal feed rate continuously. The fluidized bed feeder used caused erratic feed rates when attempts were made to feed -200 mesh coal. The solution to this problem in the past was to use a sized fraction (60 x 325 mesh) of coal. Later in the project an improved feed system was developed, based on a spouting bed feeder.

The spouting bed feeder consists of two main components, an

Figure 1. Vertical externally-heated tube furnace system.

Figure 2. Vertical externally-heated tube furnace; injector and preheater section.

Figure 3. Vertical externally-heated tube furnace;
fluidized bed feeder.

Figure 4. Bottom of vertical externally-heated tube furnace; constrictor and test substrate.

Figure 5. Pipe/cyclone ash probe.

air pump and a 1 liter Imhoff cone, and is shown in Figure 6. The pump is used to provide a circulating gas flow to agitate and transport the coal up the spouting tube. The air stream spouts the coal to the top of the feeder where it is deflected and settles down toward the take-off ports. A tangential air jet is used to fluidize the coal at the bottom of the feeder, preventing bridging and aiding coal flow to the spouting tube. The feed rate is controlled by regulating the air circulation rate and the amount of make-up air admitted. Like the fluidized bed feeder, the spouting bed feeder also rests on a top-loading balance to provide continuous monitoring of the coal feed rates.

The performance of the spouting bed feeder is generally adequate for the drop tube furnace; for example, for a desired feed rate of 0.33 g/min the deviation over a 40 minute period was 0.04 g/min. However, the feeder will intermittently clog when feeding 400 mesh coal and even some 200 mesh coals. The erratic feeding may be a problem of static charging inside the plastic cone. Glass cones may be preferable for this application. Also, when the total sample is less than 20 - 30 grams problems in fluidization produce erratic feed rates.

An additional feeder was constructed to feed consistently small (i.e., about 5 grams) of coal. This feeder is useful when only a small quantity of coal or other sample is available for combustion testing. A diagram is shown in Figure 7. The feeder uses a 6 volt DC motor and gear box to rotate a brass cylinder at

Figure 6. Spouting bed coal feeder.

Figure 7. Rotating cylinder feeder.

0 - 20 rpm. The cylinder has eight 1 mm diameter holes into which the sample is placed. As the cylinder is rotated coal falls from the holes into the funnel, where it becomes entrained in the primary air. The coal feed rate is determined by the rotational speed of the motor and the tilt of the cylinder from the horizontal position.

The coal - primary air mixture is injected into the furnace through the water-cooled injector probe. Preheated secondary air (about 3 liters/min) enters the furnace through a flow straightener. The gas velocity profiles at various axial positions at the hot zone temperature (1500°C) were calculated using a numerical computer solution of the Navier-Stokes equations. The result is shown in Figure 8. The gas stream where the injected particle resides in the primary air stream is initially decelerated in about 5 cm from the injector tip, before blending into a uniform 21.6 cm/sec velocity profile with the main stream. The gas velocity of 21.6 cm/sec was used to calculate the particle residence time in the 50 cm hot zone to be 1 to 2 seconds, assuming a 100 micron particle of density 1.5 g/cm^3 . The laminar velocity profile keeps the burning particles in a thin ray in the center of the furnace without striking the furnace walls. The gas stream and fly ash are accelerated by a constrictor (1.3 cm diameter ceramic nozzle) prior to impingement on the substrate. Exit gases are removed by a vacuum pump to prevent back-pressure build-up in the furnace tube.

Figure 8. Gas velocity profile in the vertical externally-heated tube furnace: L is the distance along the tube furnace.

The procedure for ignition and heat-up of the vertical tube furnace has been documented by Abbott.¹ The furnace was normally operated with a hot zone wall temperature of 1500° C. The gas temperature passing through the annulus around the substrate was 1100° C; the temperature "seen" by the deposit was between 1100 and 1300° C. (These temperatures were measured by using pyrometric cones, which simulate the heat transfer conditions to a cone of deposit.) The total combustion air was approximately 4 liters/minute, giving approximately 20% excess air for the pulverized coal feed rate of 0.33 grams/minute. The constrictor dimension of 1.3 cm gave gas velocities of 3 - 4 m/s. The substrate in the collector probe was maintained at 500° C before starting deposition. In tests in which data was obtained under conditions which deviated significantly from these, the specific test conditions will be described in the accompanying text.

Temperature profiles are shown in Figure 9. These temperatures were measured by a shielded suction pyrometer in the range 1450 - 1650°C.¹ The corresponding wall temperatures, from thermocouples, are also plotted. In general, the gas temperatures along the centerline of the furnace were about 30° lower than the corresponding wall temperature. The estimated particle residence times versus gas temperature are compared with a full-scale boiler firing low-rank coal in Figure 10. The particle residence times were calculated by assuming the particle velocities to be equal to the sum of the centerline gas velocity and the terminal particle velocity (from Stokes' Law). The particle residence

Figure 9. Gas-fired furnace temperature profile.

Figure 10. Estimated particle residence time versus gas temperature for the vertical tube furnace operated at 1500°C as compared to a full scale low-rank coal boiler.

times are dependent on particle size and density, and were calculated assuming an initial size of 75 micrometers and a density of 1.8 g/cm^3 when injected into the hot zone. As the coal particle burns, it decreases in size and increases in density. After the particle has passed 40 cm through the tube a size of 40 micrometers and a density of 2.5 g/cm^3 were assumed; the corresponding values for 60 cm from the point of injection were assumed to be 20 micrometers and 2.8 g/cm^3 , respectively. Thus the total particle residence time is about 2.4 seconds.

Electrically Heated Furnace

An electrical resistance furnace was designed on the same basis as the gas-fired furnace. A diagram of the electrical resistance furnace system is shown in Figure 11. The high-temperature furnace contains a 51 cm hot zone heated by 20 silicon carbide glow bars and can maintain a maximum temperature of 1550°C .

The preheat-injector system is shown in Figure 12. The system has two heating coils to heat the secondary air to a maximum of 1100°C prior to entering the main furnace. A mullite flow straightener with 1.6 mm square cells is used to provide laminar flow of secondary air from the preheat-injector system. The water-cooled injector is the same design as that of the gas-fired furnace.

Figure 11. Diagram of main electrical resistance furnace.

Figure 12. Preheater and injector system.

Examination of deposits collected on the probe or of fly ash collected without the probe showed negligible carbon content, indicating high levels of burn-out. No fly ash was collected on the furnace tube, and negligible amounts were found on the constrictor. Quadruplicate tests on 10 g lots of a Powder River Basin coal passed through the furnace in 30 minutes gave deposit masses of 313, 324, 302, and 311 mg, showing good reproducibility.

Ash Deposition Probe

The water-cooled ash deposition probe is shown in Figure 13. A machined boiler steel substrate 3.8 cm diameter by 0.64 cm thick is attached to the top of the probe. The substrate temperature is maintained at a value selected between 350 - 550°C by adjusting the cooling water flow and the tightness of the screws that hold the substrate to the probe. The temperature is monitored by a chromel-alumel thermocouple. A constrictor having a 1.27 cm nozzle is used to accelerate the gas flow to about 3-5 m/sec. The substrate is placed 2.5 cm below the constrictor.

The substrate materials are prepared from type 1040 carbon steel, supplied by the Babcock and Wilcox Company. The substrates are polished with 600 grit silicon carbide. The substrates are oxidized in air at 400°C for 20 hours to produce an oxide layer on the steel.

Figure 13. Bottom of vertical tube furnace, constrictor and ash deposition probe.

The temperature of the gases entering the constrictor can be varied between 1000 - 1300°C by adjusting the position of the constrictor or deposition probe in the base of the furnace. The vertical position of the probe in the furnace is critical; a variation of its position by 1 cm changes the temperature in the deposition region by 50°C. The gas temperature profile in the region where the deposit forms was determined using pyrometric cones ranging in melting point from 900 - 1270°C. The cones were cut to various heights and placed at various positions across the substrate. The temperature profile for a configuration with the substrate 74.1 cm from the tip of the coal injector is shown in Figure 14.

Figure 14. Temperature distribution between constrictor and substrate at 74 cm from tip of injector.

CHARACTERISTICS OF TEST COALS

The experimental work covered in this report was performed using two suites of coals. The first included the following coals: Illinois #6, Pittsburgh #8, Upper Hiawatha #1, Upper Freeport, Tunnelton, Decker, a subbituminous coal from the Powder River Region, and Texas and North Dakota lignites. Analytical data for these coals is given in Tables 1 - 6. The second suite of coals was selected from the major Western coal-bearing regions of the United States. The coals ranged in composition from having most of the ash-forming inorganic constituents organically bound to mostly present as distinct mineral phases. Complete analyses of these coals are given in Tables 7 - 9. Further, the association of the inorganic constituents was determined by chemical fractionation.² The chemical fractionation data is provided in Tables 10 - 17. When it is necessary to distinguish between sets of results obtained from one or the other of these sample suites, they will be referred to as Suite 1 and Suite 2, respectively.

Table 1. Proximate and ultimate analysis of test coals (all on a dry basis with the exception of moisture determination)*.

Coal Illinois #6 Pittsburgh #8 U.Hiawatha #1 U.Freeport Tunnelton Decker Powder River Texas N.Dakota

Rank					Basin				
	hvb	hvb	hvb	mhb	mhb	Sub.	Sub.	Lig.	Lig.
<u>Proximate</u>									
Moisture	6.8	2.0	6.4	0.8	0.6	14.0	29.6	7.6	31.7
Vol.matter	34.3	37.5	40.3	29.9	26.4	58.7	44.8	40.9	41.6
Ash	22.3	10.0	11.5	18.1	21.9	5.3	7.9	21.5	11.5
Fixed carbon	43.4	52.5	48.2	51.9	51.9	36.0	47.4	37.5	46.9
<u>Ultimate</u>									
Carbon	58.1	72.8	69.7	69.1	68.6	71.5	69.5	50.4	62.6
Hydrogen	3.8	4.5	4.1	4.3	4.1	5.0	4.7	3.8	4.3
Nitrogen	0.9	1.3	0.9	1.1	1.1	0.9	1.0	1.1	0.7
Sulfur	5.0	2.0	0.5	1.7	2.0	0.5	0.6	0.7	1.2
Oxygen (diff.)	10.0	9.4	13.4	5.8	2.2	16.9	16.3	22.5	18.7
Ash	22.3	10.0	11.5	18.1	21.9	5.3	7.9	21.5	11.5

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 2. Mineralogical analysis of LTA^{**} from test coals; n.d. = not detected, * estimated value.

Coal	Illinois #6	Pittsburgh #8	U.Hiawatha #1	U.Freeport	Tunnelton	Decker	Powder River	Texas	N.Dakota
							Basin		
LTA wt. %	22.0	11.8	12.1	21.6	22.9	5.5	9.7	23.7	14.6
<u>Minerals</u>									
quartz	25	23	28	25	22	15	15	20-25	12
pyrite	29	27	2-5	10	15	5	n.d.	1-5	5
calcite	2-5	n.d.	7	n.d.	5	6	2	n.d.	5
gypsum/									
bassinite ⁺	n.d.	n.d.	n.d.	5	n.d.	25	25	15-20	20
kaolinite	5	25	9	30	18	13	15	30-35	n.d.
illite+mixed									
layer clays	35*	10*	30*	20*	30-40*	n.d.	n.d.	n.d.	n.d.
feldspar	n.d.	n.d.	n.d.	n.d.	5-10	n.d.	n.d.	n.d.	n.d.
ankerite	n.d.	n.d.	2-5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
iron sulfate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10*

+ bassnite is often an artifact of LTA process when ashing low rank-coals.

@ Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

** low temperature ash.

Table 3. Spectrochemical analysis of high temperature ash (ASTM) of test coals.*

Coal	Illinois #6	Pittsburgh #8	U.Hawatha #1	U.Freeport	Tunnelton	Decker	River Basin	Texas	N.Dakota
Weight percent of equivalent oxides									
SiO ₂	48.3	51.1	51.1	54.1	50.3	26.2	25.8	48.7	18.7
Al ₂ O ₃	17.5	26.9	13.4	25.9	26.8	18.0	15.1	18.6	8.7
TiO ₂	0.8	0.9	0.9	1.3	1.3	1.2	0.8	1.2	0.5
Fe ₂ O ₃	20.9	15.2	6.2	9.6	11.0	7.6	7.4	5.6	13.4
MgO	0.9	0.9	2.2	1.0	1.0	3.4	5.5	2.1	5.4
CaO	4.7	0.9	14.1	1.7	2.5	15.8	24.7	9.1	18.9
MnO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Na ₂ O	0.6	0.2	2.1	0.3	0.4	8.4	1.6	0.3	9.5
K ₂ O	1.6	2.2	0.8	2.9	2.9	0.4	0.3	0.9	0.1
P ₂ O ₅	0.2	0.1	0.3	0.3	0.4	0.7	0.4	0.0	0.4
SO ₃	4.6	0.7	8.3	1.1	2.3	17.5	18.2	11.4	21.4
Total	100.0	99.1	99.4	98.2	98.9	99.2	99.8	98.0	97.0

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 4. Fusion temperature of high temperature ash (ASTM) of test coals, °C.

Coal	Illinois #6	Pittsburgh #8	U.Hiawatha #1	U.Freeport	Tunnelton	Decker	Powder River	Texas	N.Dakota Basin
<u>Oxidizing Atmosphere</u>									
Initial									
deformation	1280	1430	1170	1390	1450	1310	1270	1270	1250
Softening	1300	1460	1180	1420	1490	1330	1290	1300	1270
Hemisphere	1350	1470	1220	1450	1500	1350	1310	1350	1270
Fluid	1370	1490	1310	1480	1510	1360	1330	1380	1280
<u>Reducing Atmosphere</u>									
Initial									
deformation	1090	1310	1120	1210	1380	1130	1270	1230	1130
Softening	1120	1330	1150	1350	1410	1160	1280	1260	1180
Hemisphere	1140	1370	1180	1420	1430	1180	1290	1300	1200
Fluid	1180	1420	1220	1480	1490	1190	1300	1350	1210

Table 5. Sulfur forms of test coals. All values are "dry basis" (wt.%)*

Coal	Pyritic sulfur	Sulfate sulfur	Organic sulfur	Total sulfur
Illinois #6	1.88	0.85	2.17	4.90
Pittsburgh #8	0.76	0.22	0.89	1.87
U.Hiawatha #1	0.09	0.02	0.30	0.41
U.Freeport	0.76	0.46	0.58	1.80
Tunnelton	0.95	0.25	0.61	1.81
Decker	0.11	0.06	0.40	0.57
Powder River Basin	0.13	0.01	0.41	0.55
Texas	0.03	0.04	0.69	0.76
N.Dakota	0.06	0.70	0.39	1.15

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 6. Chloride content of test coals, wt.%*

Coal	Chloride
Illinois #6	0.06
Pittsburgh #8	0.22
U.Hiawatha #1	0.08
U.Freeport	0.32
Tunnelton	0.36
Decker	0.03
Powder River Basin	0.06
Texas	0.03
N.Dakota	0.04

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 7. Mineralogy of low-temperature ash - North Dakota lignites@.

<u>Coal</u>	<u>Indian Head</u>	<u>Beulah</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
<u>Mineralogy, %</u>						
quartz	10	4	19	31	15	20
pyrite	N.D.	8	5	<3	5	3
anhydrite ⁺	3-7	3-7	3-5	3-7	3-7	--
bassanite ⁺	25	25	20	15	15	15-25
kaolinite	3-10	6	6	7	7	8
illite and mixed layered clays*	3-15	<5	10	10	5	N.D.
calcite	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
% LTA	11.2	8.28	15.4	22.4	13.4	12.5

Note: Velva, Center, and Ion-exchanged were not analyzed due to problems interpreting results of the Mineralogy of LTA of lignite coals.

⁺ - May be an artifact of low-temperature ashing.

* - Estimated value.

@ - Analyses performed by the Mineral Constitution Laboratories, the Pennsylvania State University.

N.D. - Not detected.

Table 7. Composition of the ASTM ash - North Dakota lignites.

<u>Coal</u>	<u>Indian Head</u>	<u>Beulah</u>	<u>Velva</u>	<u>Center</u>	<u>Ion-exchanged Center</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
Ash analysis weight % as equivalent oxide (sulfur free)									
SiO ₂	21.5(25.6)	11.6(16.5)	21.6(26.0)	21.6(27.1)	31.4(35.1)	43.3(51.9)	49.9(56.8)	22.5(28.8)	29.4(38.0)
Al ₂ O ₃	12.1(14.5)	8.9(12.7)	11.1(13.4)	11.9(14.9)	17.5(19.6)	11.1(13.3)	12.0(13.7)	9.7(12.4)	13.9(18.0)
Fe ₂ O ₃	8.7(10.3)	9.0(12.8)	6.9(8.3)	11.3(14.2)	16.7(18.7)	4.6(5.5)	3.0(3.4)	5.0(6.4)	2.2(2.8)
TiO ₂	1.0(1.2)	1.0(1.4)	0.9(1.1)	0.4(0.5)	0.6(0.7)	1.4(1.7)	1.4(1.6)	0.7(0.9)	1.5(1.9)
P ₂ O ₅	0.5(0.6)	1.2(1.8)	0.5(0.6)	0.1(0.1)	0.2(0.2)	0.8(1.0)	0.8(0.9)	0.7(0.9)	1.3(1.7)
CaO	21.3(25.4)	18.9(27.0)	31.0(37.3)	20.7(26.0)	16.4(18.3)	12.5(15.0)	12.4(14.1)	24.3(31.1)	20.5(26.5)
MgO	6.6(7.9)	6.0(8.6)	8.8(10.6)	7.6(9.5)	2.9(3.2)	7.4(8.9)	4.1(4.7)	8.2(10.5)	7.2(9.3)
Na ₂ O	12.1(14.5)	13.6(19.4)	2.3(2.8)	2.9(3.6)	0.2(0.3)	1.9(2.3)	3.5(4.0)	6.9(8.8)	1.5(1.9)
K ₂ O	0.1(0.1)	0.0(0.0)	0.1(0.1)	0.6(0.8)	0.5(0.6)	0.4(0.5)	0.8(0.9)	0.1(0.1)	0.0(0.0)
SO ₃	15.9(--)	30.0(--)	16.7(--)	20.4(--)	10.6(--)	16.6(--)	12.2(--)	21.9(--)	22.6(0.0)

Table 7. Ash fusion results -- North Dakota lignites.

<u>Coal</u>	<u>Indian Head</u>	<u>Beulah</u>	<u>Velva</u>	<u>Center</u>	<u>Ion-exchanged Center</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
<u>Reducing Atmosphere, °C</u>									
initial deformation	1200	1280	1270	1240	1110	1170	1140	1010	1230
softening	1220	1350	1290	1260	1170	1180	1160	1160	1250
hemispherical	1230	1360	1290	1270	1220	1190	1200	1180	1260
fluid	1250	1370	1300	1280	1280	1220	1240	1200	1270
<u>Oxidizing Atmosphere, °C</u>									
initial deformation	1280	1310	1300	1270	1250	1180	1150	1060	1260
softening	1280	1340	1310	1270	1270	1190	1170	1180	1270
hemispherical	1290	1340	1320	1280	1310	1220	1230	1190	1270
fluid	1290	1380	1340	1280	1350	1230	1260	1210	1280

Table 8. Mineralogy of low-temperature ash - subbituminous[@].

<u>Coal</u>	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Wyodak</u>	<u>Nava jo</u>
<u>Mineralogy, %</u>				
quartz	13	19	13	23
pyrite	<3	7	<3	N.D.
anhydrite ⁺	10	3-7	10	N.D.
bassanite ⁺	25	15	25	N.D.
kaolinite	10	22	10	27
illite and mixed layered clays*	<5	<5	<5	N.D.
calcite	N.D.	N.D.	N.D.	3
montmorillonite*	N.D.	N.D.	N.D.	40
% LTA	13.2	9.95	8.45	22.0

Note: Mineralogy of LTA of Rosebud float/sink samples was not determined.

⁺ - May be an artifact of low-temperature ashing.

^{*} - Estimated value.

[@] - Analyses performed by the Mineral Constitution Laboratories, The Pennsylvania State University.

N.D. - Not detected.

Table 8. Composition of the ASTM ash - subbituminous.

<u>Coal</u>	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Rosebud 1.4 Float</u>	<u>Rosebud 1.6 Float</u>	<u>Rosebud 1.6 Sink</u>	<u>Wyodak</u>	<u>Nava jo</u>
Ash analysis weight % as equivalent oxide (sulfur free)							
SiO ₂	29.1(37.0)	38.2(44.7)	31.9(36.8)	45.5(48.9)	44.9(48.9)	23.8(30.6)	54.6(56.9)
Al ₂ O ₃	11.5(14.6)	19.4(22.7)	21.5(24.8)	24.7(26.6)	19.1(20.8)	14.8(19.1)	26.4(27.5)
Fe ₂ O ₃	6.6(8.4)	5.9(6.9)	1.3(1.5)	1.3(1.4)	18.6(20.2)	6.6(8.5)	5.3(5.5)
TiO ₂	0.6(0.8)	1.3(1.5)	1.2(1.4)	1.2(1.3)	1.3(1.4)	1.2(1.5)	1.2(1.3)
P ₂ O ₅	0.6(0.8)	0.7(0.8)	1.0(1.2)	0.5(0.5)	0.3(0.3)	1.5(1.9)	0.2(0.2)
CaO	26.0(33.0)	13.6(15.9)	19.6(22.6)	13.8(14.8)	6.0(6.5)	22.8(29.4)	4.2(4.4)
MgO	3.9(5.0)	5.6(6.6)	9.5(10.9)	6.0(6.5)	1.6(1.7)	5.9(7.6)	1.9(2.0)
Na ₂ O	0.0(0.0)	0.5(0.6)	0.8(0.9)	0.0(0.0)	0.0(0.0)	0.7(0.9)	1.3(1.4)
K ₂ O	0.4(0.5)	0.3(0.4)	0.0(0.0)	0.0(0.0)	0.1(0.1)	0.3(0.4)	0.7(0.7)
SO ₃	21.3(--)	14.6(--)	13.2(--)	7.0(--)	8.1(--)	22.4(--)	4.1(0.0)

Table 8. Ash fusion results - subbituminous.

<u>Coal</u>	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Rosebud 1.4 Float</u>	<u>Rosebud 1.6 Float</u>	<u>Rosebud 1.6 Sink</u>	<u>Wyodak</u>	<u>Navajo</u>
<u>Reducing Atmosphere, °C</u>							
initial deformation	1170	1210	1180	1250	1210	1170	1430
softening	1190	1240	1200	1310	1240	1190	1490
hemispherical	1210	1310	1340	1330	1250	1210	1500
fluid	1220	1330	1390	1370	1260	1220	1530
<u>Oxidizing Atmosphere, °C</u>							
initial deformation	1210	1230	1200	1280	1230	1200	1440
softening	1210	1260	1220	1330	1260	1210	1500
hemispherical	1220	1340	1360	1340	1270	1250	1510
fluid	1240	1360	1410	1380	1270	1280	1540

Table 9. Composition of ASTM ash - Texas lignites.

<u>Coal</u>	<u>San Miguel</u>	<u>Ion-exchanged San Miguel</u>	<u>Martin Lake</u>
Ash analysis weight % as equivalent oxide <u>(sulfur free)</u>			
SiO ₂	52.8(59.3)	70.4(72.3)	19.9(26.1)
Al ₂ O ₃	14.6(16.4)	17.1(17.6)	11.9(15.6)
Fe ₂ O ₃	4.8(5.3)	5.5(5.6)	16.1(21.0)
TiO ₂	0.8(0.9)	0.8(0.8)	0.9(1.1)
P ₂ O ₅	0.3(0.4)	0.1(0.1)	0.7(0.9)
CaO	7.9(8.8)	2.6(2.7)	16.2(21.1)
MgO	0.8(0.9)	0.3(0.3)	7.5(9.7)
Na ₂ O	4.8(5.3)	0.1(0.1)	3.2(4.2)
K ₂ O	2.4(2.7)	0.5(0.5)	0.3(0.4)
SO ₃	10.9(--)	2.4(--)	23.5(--)

Table 9. Ash fusion results - Texas lignite.

<u>Coal</u>	<u>San Miguel</u>	<u>Ion-exchanged San Miguel</u>	<u>Martin Lake</u>
<u>Reducing Atmosphere, °C</u>			
initial deformation	1180	1260	1250
softening	1200	1300	1270
hemispherical	—	1320	1280
fluid	1370	1390	1280
<u>Oxidizing Atmosphere, °C</u>			
initial deformation	1200	1250	1280
softening	1240	1260	1300
hemispherical	1390	1380	1300
fluid	1400	1410	1310

CHEMICAL FRACTIONATION DATA

Table 10. Concentration of inorganic elements in North Dakota lignites on a dry coal basis (parts per million).

	<u>Indian Head</u>	<u>Beulah</u>	<u>Velva</u>	<u>Center Center</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
Na	6221	4620	N.D.	3180	1243	4730	5000	720
Mg	9690	980		7910	4970	5010	4870	5060
Al	4940	2880		5580	5240	11480	8140	8870
Si	7060	7760		11540	13690	33060	12550	15190
K	1150	--		1340	390	1530	680	200
Ca	15560	7770		13630	17400	14070	19550	33670
Ti	400	104		330	430	1060	370	500
Fe	6810	4800		9640	5300	2810	3420	4340

N.D. - No Data

Table 11. Percentage of the element associated in the North Dakota lignites as a cation extractable with 1 M ammonium acetate.

	<u>Indian Head</u>	<u>Beulah</u>	<u>Velva</u>	<u>Center</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
Na	76	99	N.D.	100	100	100	100	79
Mg	19	85		100	92	88	98	99
Al	0	0		0	0	0	0	0
Si	1	0		2	0	0	0	0
K	2	N.A.		32	9	3	7	N.A.
Ca	39	73		81	74	75	71	78
Ti	0	0		2	0	0	5	0
Fe	0	0		0	0	0	0	0

N.D. - No Data

N.A. - Not Analyzed

Table 12. Percentage of the element associated in the North Dakota lignites possibly as a coordinated species, carbonate, or hydroxide that is extractable with 1 M HCl.

	<u>Indian Head</u>	<u>Beulah</u>	<u>Velva</u>	<u>Center</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
Na	0	0	N.D.	0	1	0	0	8
Mg	1	15		0	4	5	2	3
Al	51	80		53	52	31	32	50
Si	14	6		11	2	2	0	8
K	1	N.A.		25	0	0	0	N.A.
Ca	12	18		16	14	24	29	17
Ti	2	10		26	29	8	16	8
Fe	40	45		29	38	29	32	24

N.D. - No Data

N.A. - Not Analyzed

Table 13. Percentage of the element remaining in the North Dakota lignites after extraction with ammonium acetate and hydrochloric acid. These elements are probably associated within the coal matrix as insoluble clay minerals, quartz, and sulfides.

	<u>Indian Head</u>	<u>Beulah</u>	<u>Velva</u>	<u>Center</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
Na	24	0	N.D.	0	0	0	0	13
Mg	80	0		0	0	7	0	0
Al	49	19		47	48	69	68	50
Si	85	94		87	98	98	100	92
K	97	N.A.		43	91	97	93	N.A.
Ca	49	8		3	12	1	0	4
Ti	98	89		72	90	98	79	92
Fe	60	55		71	62	71	68	76

N.D. - No Data

N.A. - Not Analyzed

Table 14. Concentration of elements in subbituminous coals and Texas lignites (parts per million).

	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Wyodak</u>	<u>Navajo</u>	<u>San Miguel</u>	<u>Martin Lake</u>
Na	N.D.	N.A.	N.D.	2500	7300	964
Mg		4500		970	600	11510
Al		7940		26000	14400	4630
Si		14330		38000	35800	7920
K		N.A.		960	970	993
Ca		10660		3000	8210	15530
Ti		581		950	530	203
Fe		3090		4500	4400	11090

N.D. - No Data

N.A. - Not Analyzed

Table 15. Percentage of the element in the subbituminous coals and Texas lignites associated as cations extractable with 1 M ammonium acetate.

	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Wyodak</u>	<u>Navajo</u>	<u>San Miguel</u>	<u>Martin Lake</u>
Na	N.D.	N.A.	N.D.	82	100	98
Mg		100		31	100	17
Al		0		0	0	0
Si		0		0	0	0
K		N.A.		6	53	2
Ca		83		72	71	52
Ti		0		0	0	0
Fe		0		0	0	28

N.D. - No Data

N.A. - Not Analyzed

Table 16. Percentage of the elements in the subbituminous coals and Texas lignites possibly associated as coordinated species, carbonates, or hydroxides that are extractable with hydrochloric acid.

	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Wyodak</u>	<u>Nava jo</u>	<u>San Miguel</u>	<u>Martin Lake</u>
Na	N.D.	N.A.	N.D.	3	0	2
Mg		0		44	0	1
Al		29		13	11	54
Si		6		10	0	12
K		N.A.		9	9	2
Ca		15		21	27	21
Ti		27		2	15	2
Fe		14		68	41	21

N.D. - No Data

N.A. - Not Analyzed

Table 17. Percentage of the element remaining in the subbituminous coals and Texas lignites after extraction with ammonium acetate and hydrochloric acid. These elements are probably associated within the coal matrix as insoluble clay minerals, quartz, and sulfides.

	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Wyodak</u>	<u>Navajo</u>	<u>San Miguel</u>	<u>Martin Lake</u>
Na	N.D.	N.A.	N.D.	15	0	0
Mg		0		25	0	82
Al		71		87	88	46
Si		94		90	100	88
K		N.A.		85	38	96
Ca		2		7	2	27
Ti		73		98	85	98
Fe		86		32	59	79

N.D. - No Data

N.A. - Not Analyzed

CHARACTERISTICS OF DEPOSITS PRODUCED IN A LABORATORY FURNACE

The general structure of a deposit consists of four distinct regions:

1. Dust, which typically consists of fine spheres (mainly 2 - 5 microns) covering the substrate surface but which could not be easily blown from the surface.
2. The lower portion of the deposit mass, which consists mainly of 10 - 15 micron spheres loosely sintered together, with substantial porosity.
3. The upper portion of the deposit mass, consisting of 25-50 micron spheres which were definitely fused together and which had less porosity than the lower portion of the deposit.
4. The top portion of the deposit, in which the material appears to be almost completely fused, with evidence of crystallization from a melt.

Each of these regions will be discussed in detail in the subsections which follow.

The general structures of the deposits obtained from the Suite 1 coals are compared in Table 18. The results of analysis of selected regions of these deposits are summarized in Table 19. The Fe_2O_3 content of the deposits from all the high-rank coals except Upper Hiawatha #1 was higher than that in the ASTM ash.

Table 18. Comparison of structure of deposits.

Coal	Dust material	Lower portion of deposit mass	Upper portion of deposit mass	Top of deposit mass
Illinois #6 U.Hiawatha #1 U.Freeport Texas	Weak, no sintering, no fusion.	Weak, slightly sintered, no fusion.	Strong, highly sintered, no fusion.	Very strong, fused.
Powder River- Basin N.Dakota	Weak, no sintering, no fusion, but sticky.	Same as above.	Strong, moderated sintering, no fusion.	Strong, fused.
Tunnelton Pittsburgh #8	Weak, no sintering, no fusion.	Same as above.	Less strong than above; moderated sintering, no fusion.	Strong, highly sintered, fused.

Table 19. Spectrochemical analysis of high temperature ash (ASTM) and deposit from Upper Freeport coal.*

	High temperature ash	Dust material and lower portion of deposit mass	Upper portion of deposit mass
Weight percent of equivalent oxides (SO ₃ free basis)			
SiO ₂	54.1 (55.7)	51.1 (51.2)	51.6 (52.6)
Al ₂ O ₃	25.9 (26.7)	25.7 (25.8)	25.6 (26.0)
TiO ₂	1.3 (1.3)	1.5 (1.5)	1.4 (1.4)
Fe ₂ O ₃	9.6 (9.9)	15.8 (15.8)	15.5 (15.7)
MgO	1.0 (1.0)	1.0 (1.0)	1.0 (1.0)
CaO	1.7 (1.8)	1.8 (1.8)	1.6 (1.6)
SrO	0.0 (0.0)	0.1 (0.1)	0.1 (0.1)
BaO	0.0 (0.0)	0.1 (0.1)	0.1 (0.1)
Na ₂ O	0.3 (0.3)	0.4 (0.4)	0.2 (0.2)
K ₂ O	2.9 (3.0)	2.3 (2.3)	2.2 (2.2)
P ₂ O ₅	0.3 (0.3)	0.0 (0.0)	0.0 (0.0)
SO ₃	1.1 (—)	0.1 (—)	0.1 (—)
Total	98.2	99.9	98.5

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 19. Spectrochemical analysis of high temperature ash
(ASTM) from Illinois #6 coal.*

	High temperature ash	Upper portion of deposit mass
Weight percent of equivalent oxides (SO ₃ free basis).		
SiO ₂	48.3 (50.6)	52.1 (52.1)
Al ₂ O ₃	17.5 (18.3)	18.9 (18.9)
TiO ₂	0.8 ((0.8)	0.8 (0.8)
Fe ₂ O ₃	20.9 (21.9)	21.3 (21.3)
MgO	0.8 (0.9)	1.0 (1.0)
CaO	4.7 (4.9)	4.0 (4.0)
Na ₂ O	0.6 (0.6)	0.5 (0.5)
K ₂ O	1.6 (1.7)	1.6 (1.6)
P ₂ O ₅	0.2 (0.2)	0.0 (0.0)
SO ₃	4.6 (--)	0.1 (--)
Total	101.1	100.3

*Source = Mineral Constitution Laboratories, The Pennsylvania
State University, Pa.

Table 19. Spectrochemical analysis of high temperature ash
(ASTM) from Tunnelton coal.*

	High temperature ash	Upper portion of deposit mass
	Weight percent of equivalent oxides (SO ₃ free basis)	
SiO ₂	50.3 (51.5)	52.8 (52.7)
Al ₂ O ₃	26.8 (27.4)	25.7 (25.7)
TiO ₂	1.3 (1.3)	1.1 (1.1)
Fe ₂ O ₃	11.0 (11.3)	14.5 (14.5)
MgO	1.0 (1.0)	1.1 (1.1)
CaO	2.5 (2.6)	2.6 (2.6)
SrO	0.0 (0.0)	0.1 (0.1)
BaO	0.0 (0.0)	0.1 (0.1)
Na ₂ O	0.4 (0.4)	0.4 (0.4)
K ₂ O	2.9 (3.0)	2.2 (2.2)
P ₂ O ₅	0.4 (0.4)	0.0 (0.0)
SO ₃	2.3 (—)	0.1 (—)
Total	98.9	100.0

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 19. Spectrochemical analysis of high temperature ash
(ASTM) from Pittsburgh #8 coal.*

High temperature ash Upper portion of deposit mass		
Weight percent of equivalent oxides (SO ₃ free basis)		
SiO ₂	51.1 (51.5)	45.7 (45.7)
Al ₂ O ₃	26.9 (27.0)	23.5 (23.5)
TiO ₂	0.9 (0.9)	1.0 (1.0)
Fe ₂ O ₃	15.2 (15.3)	18.6 (18.6)
MgO	0.6 (0.6)	0.7 (0.7)
CaO	0.9 (0.9)	1.2 (1.2)
SrO	0.0 (0.0)	0.1 (0.1)
BaO	0.0 (0.0)	0.1 (0.1)
Na ₂ O	0.2 (0.2)	0.3 (0.3)
K ₂ O	2.2 (2.2)	1.7 (1.7)
P ₂ O ₅	0.1 (0.1)	0.0 (0.0)
SO ₃	0.7 (—)	0.1 (—)
Total	99.1	93.0

*Source = Mineral Constitution Laboratories, The Pennsylvania
State University, Pa.

Table 19. Spectrochemical analysis of high temperature ash (ASTM) from Upper Hiawatha #1 coal.*

	High temperature ash	Dust material and lower portion of deposit mass	Upper portion of deposit mass	Top portion of deposit mass	Upper portion of deposit mass
		normal constrictor			60° angle constrictor
	Weight percent of equivalent oxides (SO ₃ free basis)				
SiO ₂	51.1 (55.7)	58.5 (59.3)	63.7 (63.8)	65.6 (65.8)	63.2 (63.3)
Al ₂ O ₃	13.4 (14.6)	14.6 (14.8)	14.7 (14.7)	15.0 (15.0)	15.5 (15.5)
TiO ₂	0.9 (1.0)	0.8 (0.8)	0.8 (0.8)	0.8 (0.8)	0.8 (0.8)
Fe ₂ O ₃	6.2 (6.8)	6.0 (6.1)	5.3 (5.3)	4.8 (4.8)	5.3 (5.3)
MgO	2.2 (2.4)	2.0 (2.0)	1.9 (1.9)	1.7 (1.7)	1.9 (1.9)
CaO	14.1 (15.4)	13.4 (13.6)	11.0 (11.0)	10.1 (10.1)	10.7 (10.7)
SrO	0.0 (0.0)	0.1 (0.1)	0.1 (0.1)	0.1 (0.1)	0.1 (0.1)
BaO	0.0 (0.0)	0.1 (0.1)	0.1 (0.1)	0.0 (0.0)	0.1 (0.1)
Na ₂ O	2.1 (2.3)	2.3 (2.3)	0.7 (0.7)	1.5 (1.5)	1.6 (1.6)
K ₂ O	0.8 (0.9)	0.8 (0.8)	0.8 (0.8)	0.8 (0.8)	0.7 (0.7)
P ₂ O ₅	0.3 (0.3)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
SO ₃	8.3 (—)	1.3 (—)	0.1 (—)	0.1 (—)	0.1 (—)

*Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 19. Spectrochemical analysis of high temperature ash (ASTM) from North Dakota lignite.*

	High temperature ash	Upper portion of deposit mass (normal constrictor)	Upper portion of deposit mass (60° angle constrictor)
Weight percent of equivalent oxides (SO ₃ free basis)			
SiO ₂	18.7 (23.8)	30.0 (30.1)	28.6 (29.1)
Al ₂ O ₃	8.7 (11.1)	13.0 (13.1)	13.5 (13.7)
TiO ₂	0.5 (0.6)	0.6 (0.6)	0.7 (0.7)
Fe ₂ O ₃	13.4 (17.0)	13.2 (13.4)	9.8 (10.0)
MgO	5.4 (6.9)	7.9 (7.9)	7.9 (8.0)
CaO	18.9 (24.0)	29.0 (29.1)	30.0 (30.5)
SrO	0.0 (0.0)	1.1 (1.1)	0.0 (0.0)
BaO	0.0 (0.0)	1.9 (1.9)	0.0 (0.0)
Na ₂ O	9.5 (12.1)	3.1 (3.1)	3.1 (3.2)
K ₂ O	0.1 (0.1)	0.2 (0.2)	0.2 (0.2)
P ₂ O ₅	0.4 (0.5)	0.0 (0.0)	0.0 (0.0)
SO ₃	21.4 (—)	0.6 (—)	1.6 (—)
Total	97.0	100.6	95.4

*Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 19. Spectrochemical analysis of high temperature ash (ASTM) from Texas lignite.*

	High temperature ash	Dust material and lower portion of deposit mass	Upper portion of deposit mass	Top portion of deposit mass
Weight percent of equivalent oxides (SO ₃ free basis)				
SiO ₂	48.7 (55.0)	49.7 (50.0)	57.7 (57.8)	58.3 (58.4)
Al ₂ O ₃	18.6 (21.0)	21.5 (21.7)	22.5 (22.5)	23.4 (23.4)
TiO ₂	1.2 (1.4)	1.8 (1.8)	1.7 (1.7)	1.7 (1.7)
Fe ₂ O ₃	5.6 (6.3)	4.2 (4.2)	3.4 (3.4)	3.5 (3.5)
MgO	2.1 (2.3)	3.4 (3.4)	2.3 (2.3)	2.3 (2.3)
CaO	9.1 (10.3)	16.5 (16.6)	10.7 (10.7)	9.8 (9.8)
SrO	0.0 (0.0)	0.2 (0.2)	0.2 (0.2)	0.2 (0.2)
BaO	0.0 (0.0)	0.2 (0.2)	0.1 (0.1)	0.1 (0.1)
Na ₂ O	0.3 (0.3)	0.9 (0.9)	0.4 (0.4)	0.4 (0.4)
K ₂ O	0.9 (1.0)	0.5 (0.5)	0.7 (0.7)	0.7 (0.7)
P ₂ O ₅	0.1 (0.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
SO ₃	11.4 (—)	0.7 (—)	0.2 (—)	0.1 (—)
Total	98.0	99.7	99.8	100.5

*Source - Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 19. Spectrochemical analysis of high temperature ash (ASTM)
from Powder River Basin Coal.*

	High temperature ash	Dust material and lower portion of deposit mass	Upper portion of deposit mass (normal constrictor)	Upper portion of deposit mass (60° angle constrictor)
Weight percent of equivalent oxides (SO ₃ free basis)				
SiO ₂	25.8 (31.5)	20.4 (20.8)	36.0 (36.1)	27.7 (28.0)
Al ₂ O ₃	15.1 (18.5)	17.8 (18.2)	19.2 (19.2)	18.8 (19.0)
TiO ₂	0.8 (1.0)	1.0 (1.0)	1.0 (1.0)	1.0 (1.0)
Fe ₂ O ₃	7.4 (9.0)	6.5 (6.6)	6.8 (6.8)	5.5 (5.6)
MgO	5.5 (6.7)	8.1 (8.3)	6.6 (6.6)	6.6 (6.7)
CaO	24.7 (30.2)	34.1 (34.8)	30.0 (30.0)	31.0 (31.3)
MnO	0.0 (0.0)	0.1 (0.1)	0.1 (0.1)	0.0 (0.0)
SrO	0.0 (0.0)	0.6 (0.6)	0.5 (0.5)	0.5 (0.5)
BaO	0.0 (0.0)	0.3 (0.3)	0.3 (0.3)	0.3 (0.3)
Na ₂ O	1.6 (2.0)	0.8 (0.8)	0.4 (0.4)	0.7 (0.7)
K ₂ O	0.3 (0.3)	0.2 (0.2)	0.2 (0.2)	0.3 (0.3)
P ₂ O ₅	0.4 (0.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
SO ₃	18.2 (—)	2.0 (—)	0.1 (—)	1.1 (—)
Total	99.8	91.9	101.2	93.2

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 19. Spectrochemical analysis of high temperature ash (ASTM) from Decker coal.*

	High temperature ash	Upper portion of deposit mass
Weight percent of equivalent oxides (SO ₃ free basis)		
SiO ₂	26.2 (31.8)	49.5 (49.7)
Al ₂ O ₃	18.0 (21.8)	24.6 (24.7)
TiO ₂	1.2 (1.5)	1.2 (1.2)
Fe ₂ O ₃	7.6 (9.2)	11.5 (11.6)
MgO	3.4 (4.1)	1.2 (1.2)
CaO	15.8 (19.2)	4.6 (4.6)
SrO	0.0 (0.0)	0.3 (0.3)
BaO	0.0 (0.0)	0.3 (0.3)
Na ₂ O	8.4 (10.2)	0.9 (0.9)
K ₂ O	0.4 (0.5)	1.6 (1.6)
P ₂ O ₅	0.7 (0.8)	0.0 (0.0)
SO ₃	17.5 (--)	0.3 (--)
Total	99.2	96.4

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

This trend was not observed for the low-rank coals in Suite 1, with the sole exception of Decker. Changes in SiO_2 concentration were relatively small for the high-rank coals, with the exception again of the Upper Hiawatha #1. SiO_2 concentration within the deposit was essentially constant irrespective of position within the deposit. On the other hand, the deposits from low-rank coals showed higher SiO_2 concentrations than their respective ASTM ashes, except for the Powder River subbituminous coal. Trends in SiO_2 concentration tracked those of CaO , suggesting that CaO may react with quartz or clays to form calcium silicates or aluminosilicates which make the ashes sticky and thus more prone to deposit. Changes in Al_2O_3 concentration were relatively small; the concentration appeared to remain essentially constant irrespective of position in the deposit, type of coals, or composition of the ASTM ash. This finding may indicate that most of the clays invariable participate in the ash deposit build-up for most of the tested coals. The ASTM ashes had, with the exception of the Texas lignite, higher Na_2O concentrations than the respective deposits, indicating that most of the sodium vaporizes in the coal flame under the conditions of the drop-tube furnace. Significant amounts of sodium and sulfur species were found concentrated in the dust around the edge of the substrate and along the cooled collecting probe near the furnace exit, suggesting that most of the sodium and sulfur follow the flue gas stream and condense in the cooler regions.

A synthetic coal with a starting mineral composition

corresponding to Illinois #6 was prepared with a mineral mixture of 29% pyrite, 5% calcite, 25% quartz, 5% kaolinite, and 35% illite. Figures 15 and 16 compare the SEM photomicrographs of the deposits from the synthetic coal and the actual Illinois #6 coal. These figures show the similarity of deposit structure at different locations on the deposits. The EDS spectra showed the same types of compositions of the deposit spheres. It appears that calcite caused the fusion of most constituents in the synthetic coal. There were some irregular quartz particles that did not fuse into fly ash spheres. X-ray diffraction analysis confirmed these observations: at the top of the deposit there were phases containing silicon and aluminum (anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, and augite, $\text{Ca}(\text{Fe},\text{Mg})\text{Si}_2\text{O}_6$), showing that the melted top of the deposit did add calcite, clays and quartz in a manner similar to that of the actual coal.

A typical deposit formed from Suite 2 coals is shown in Figure 17. Deposits could grow to heights of more than 20 mm in 15 - 30 min. The deposits characteristically have strongly adherent particles, a thin dust layer, a base, and a deposit mass with growth lines in the direction of the oncoming gas flow. The shape, color, and quantity of the deposit are coal-dependent. The consistency ranged from lightly sintered, highly porous deposits to strongly sintered, dense ones. Qualitative descriptions of the deposits formed in selected tests are given in Tables 20 - 22.

The composition of deposits formed from Suite 2 coals was compared to the composition of the corresponding ashes prepared

Figure 15. SEM photomicrographs of deposit from synthetic Illinois #6 coal; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top portion of deposit mass.

Figure 15 continued. SEM photomicrographs of (a) adherent material; and (b) collected fly ash from filter; both materials from Synthetic Illinois #6 coal.

Figure 16. SEM photomicrographs of deposit from Illinois #6 coal; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top portion of deposit mass.

Figure 16 continued. SEM photomicrographs of (a) adherent material; and (b) collected fly ash from filter; both materials from Illinois #6 coal.

DESCRIPTION OF THE DEPOSITS

Figure 17. Typical deposit formed from a North Dakota lignite.

Table 20. Qualitative description of deposits from North Dakota lignites.

<u>Coal</u>	<u>Indian Head</u>	<u>Beulah</u>	<u>Velva</u>
Deposit height, mm	16	15	15
Deposit top half	dark brown small amount of fusing (3.0mm)	dark brown no fusing (7.5mm)	brown no fusing (10mm)
Deposit lower half	dark brown no fusing highly sintered (5mm)	dark brown no fusing slightly sintered (6mm)	brown no fusing sintered (4mm)
Base layer	brown to tan slightly sintered (5mm)	brown to green slightly sintered (1.5mm)	brown slightly sintered (1mm)
Thin dust layer	white to tan abundant (3mm)	white to tan	tan
Adherent material	very little	very little	very little

Table 20. Continued.

<u>Coal</u>	<u>Center (1500°C)</u>	<u>Ion-exchanged Center (1500°C)</u>	<u>Center (1400°C)</u>	<u>Ion-exchanged Center (1400°C)</u>
Deposit height, mm	16	20	19	20
Deposit top half	dark brown completely fused (7mm)	light brown no fusing (8mm)	brown no fusing (8mm)	light brown no fusing (6mm)
Deposit lower half	dark brown no fusing (9mm)	light brown sintered (6mm)	brown sintered (5mm)	light brown sintered (9mm)
Base layer	brown to tan very little	brown to tan little	brown to tan little	brown to tan abundant
Thin dust layer	white very little	white little	white abundant	white abundant
Adherent material	abundant	very little	little	very little

Table 20. Continued.

<u>Coal</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
Deposit height, mm	16	17.5	15	15
Deposit top half	glassy highly fused tan (6mm)	glassy fused highly porous tan (5mm)	slightly glassy fused dark brown (10mm)	glassy highly porous tan (10mm)
Deposit lower half	sintered no fusing (9mm)	sintered no fusing (10.5mm)	sintered no fusing (6mm)	sintered no fusing (4mm)
Base layer	slightly sintered tan to white	slightly sintered tan	slightly sintered tan	slightly sintered tan to white
Thin dust layer	white	white	white	white
Adherent material	little	little	little	little

Table 21. Qualitative description of subbituminous deposits.

<u>Coal</u>	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Rosebud 1.4 Float</u>	<u>Rosebud 1.6 Float</u>	<u>Rosebud 1.6 Sink</u>	<u>Wyodak</u>	<u>Navajo</u>
Deposit height, mm	14	19	12	12	20	13	12
Deposit top half	no fusing grey (6mm)	no fusing grey to tan (11mm)	fused, glassy white (4mm)	no fusing grey (8mm)	no fusing grey to tan (10mm)	no fusing grey (6mm)	no fusing grey (6mm)
Deposit lower half	lightly sintered grey (5mm)	lightly sintered grey (6mm)	highly sintered white (6mm)	no fusing grey (3mm)	no fusing grey to tan (6mm)	lightly sintered grey (5mm)	lightly sintered grey (5mm)
Base layer	none	yellow to gold	white	grey to white	grey to white	tan	tan to white
Thin dust layer	white	white	white	white	grey to white	white	white
Adherent material	very little	little	very little	little	abundant	little	little

Table 22. Qualitative description of Texas lignite deposits.

<u>Coal</u>	<u>San Miguel (1500°C)</u>	<u>Ion-exchanged San Miguel (1500°C)</u>	<u>San Miguel (1400°C)</u>	<u>Ion-exchanged San Miguel (1400°C)</u>	<u>Martin Lake</u>
Deposit height, mm	14	18	13	17	13
Deposit top half	grey fused porous (5mm)	grey-tan sintered. (8mm)	grey-tan very lightly sintered (6mm)	tan very soft deposit (7mm)	brown highly sintered (6mm)
Deposit lower half	grey-tan sintered (6mm)	grey lightly sintered (8mm)	grey-tan sintered (5mm)	grey-tan lightly sintered (7mm)	brown-tan sintered (4mm)
Base	grey lightly sintered	grey very lightly sintered	grey lightly sintered	grey very lightly sintered	tan lightly sintered
Thin dust layer	white very little	grey-white very little	grey-white little	white very little	tan little
Adherent material	abundant	little	little	little	little

under standard ASTM conditions. The results of this comparison are given in Tables 23 - 26. The most striking difference is the lower concentration of sodium and sulfur in the deposit. This difference may be due to these species remaining in the gas phase at the high gas temperatures (1264°C) passing through the constrictor or that the sodium and sulfur concentrate in the smaller size fractions and are more likely to follow gas streamlines without being deposited. The concentration of silicon appears higher in most deposits than in the ash. This may be due to large particles of silica impacting the substrate or the deposit. The concentrations of iron and calcium are lower in the deposit than in the ash in most cases. The lower calcium concentration may be due to the fact that most of the calcium is organically bound and thus more likely to occur in the smaller particle sizes, behaving similarly to sodium and sulfur. Iron is an anomaly; the concentration of iron would be expected to be higher in the deposit than in the ash because the high density of iron particles increases the possibility of impacting the deposit and substrate.

The variation in composition across a deposit formed from Indian Head lignite was determined by SEM-EDS analysis. Sodium decreases from the base of the deposit to the top and in most cases decreases from the centerline to the outer edge. These trends are thought due to the relative volatility of sodium-containing species and that particles containing higher concentrations of sodium stick more readily and thus are

Table 23. Composition of bulk North Dakota lignite deposits compared to ASTM ash (weight percent as equivalent oxide SO₃ free basis).

Oxide	Indian Head		Beulah		Velva		Center		I/E ⁺ Center	
	ASTM Ash	Bulk Deposit	ASTM Ash	Bulk Deposit	ASTM Ash	Bulk Deposit	ASTM Ash	Bulk Deposit	ASTM Ash	Bulk Deposit
SiO ₂	25.6	23.2	16.5	34.8	26.0	38.8	27.1	31.1	35.1	40.6
Al ₂ O ₃	14.5	16.6	12.7	14.7	13.4	14.0	14.9	17.3	19.6	22.0
Fe ₂ O ₃	10.3	9.3	12.8	10.8	8.3	5.9	14.2	11.7	18.7	13.0
TiO ₂	1.2	1.1	1.4	0.4	1.1	0.3	0.5	0.5	0.7	0.7
P ₂ O ₅	0.6	0.3	1.8	0.3	0.6	0.0	0.1	0.1	0.2	0.0
CaO	25.4	35.7	12.0	30.3	37.3	30.3	26.0	23.8	18.3	18.9
MgO	7.9	6.9	8.6	3.4	10.6	9.2	9.5	13.7	3.2	3.6
Na ₂ O	14.5	6.9	19.4	5.0	2.8	1.4	3.6	2.4	0.3	0.7
K ₂ O	0.1	0.0	0.0	0.2	0.1	0.1	0.8	0.4	0.6	0.5
SO ₃ [*]	15.9	5.2	30.0	4.6	16.7	3.3	20.4	2.9	10.6	1.5

* - SO₃ included for comparison purposes.

⁺ - I/E = Ion exchanged.

Table 24. Composition of bulk Gascoyne lignite deposits compared to ASTM ash
(weight percent as equivalent oxide SO_3 free basis).

<u>Oxide</u>	<u>Red</u>		<u>White</u>		<u>Blue</u>		<u>Yellow</u>	
	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>
SiO_2	51.9	68.2	56.8	67.6	28.8	45.3	38.0	48.0
Al_2O_3	13.3	9.8	13.7	8.7	12.4	11.3	18.0	17.8
Fe_2O_3	5.5	3.1	3.4	4.7	6.4	4.3	2.8	2.3
TiO_2	1.7	1.3	1.6	0.9	0.9	0.5	1.9	1.4
P_2O_5	1.0	0.0	0.9	0.0	0.9	0.0	1.7	0.2
CaO	15.0	11.2	14.1	12.1	31.0	29.7	26.5	21.5
MgO	8.9	2.1	4.7	1.9	10.5	5.5	9.3	9.0
Na_2O	2.3	1.4	4.0	3.6	8.8	3.6	1.9	0.7
K_2O	0.5	0.3	0.9	0.4	0.1	0.3	0.0	0.1
SO_3	16.6	2.9	12.2	2.8	21.4	2.8	22.6	2.8

Table 29. Composition of bulk subbituminous coal deposits compared to ASTM ash (weight percent as equivalent oxide SO_3 free basis).

Oxide	<u>Dave Johnston</u>		<u>Rosebud</u>		<u>Rosebud 1.4 Float</u>		<u>Wyodak</u>		<u>Navajo</u>	
	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>
SiO_2	37.0	58.7	44.7	55.9	36.8	46.7	30.6	47.7	56.9	64.5
Al_2O_3	14.6	15.4	22.7	24.0	24.8	26.7	19.1	17.1	27.5	23.2
Fe_2O_3	8.4	5.8	6.9	5.0	1.5	0.9	8.5	4.8	5.5	4.1
TiO_2	0.8	0.7	1.5	0.8	1.4	1.0	1.5	0.9	1.3	1.0
P_2O_5	0.8	0.0	0.8	0.5	1.2	0.1	1.9	0.3	0.2	0.2
CaO	33.0	16.7	15.9	12.1	22.6	16.2	29.4	26.1	4.4	4.0
MgO	5.0	1.2	6.6	2.2	10.9	8.6	7.6	2.3	2.0	2.1
Na_2O	0.0	0.3	0.6	0.3	0.9	0.2	0.9	0.4	1.4	1.0
K_2O	0.5	1.2	0.4	0.2	0.0	0.2	0.4	0.4	0.0	0.0
SO_3	21.3	2.7	14.6	2.6	13.2	2.8	22.4	3.5	4.1	1.5

Table 26. Composition of bulk Texas lignite deposits compared to ASTM ash (weight percent as equivalent oxide SO₃ free basis).

<u>Oxide</u>	<u>San Miguel</u>		<u>I/E San Miguel</u>		<u>Martin Lake</u>	
	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>	<u>ASTM</u> <u>Ash</u>	<u>Bulk</u> <u>Deposit</u>
SiO ₂	59.3	64.5	72.3	77.4	26.1	39.0
Al ₂ O ₃	16.4	15.4	17.6	16.2	15.6	15.4
Fe ₂ O ₃	5.3	4.2	5.6	4.0	21.0	12.2
TiO ₂	0.9	0.8	0.8	0.9	1.1	0.0
P ₂ O ₅	0.4	0.2	0.1	0.2	0.9	0.4
CaO	8.8	7.6	2.7	1.0	21.1	16.7
MgO	0.9	0.8	0.3	0.2	9.7	2.9
Na ₂ O	5.3	4.2	0.1	0.0	4.2	0.8
K ₂ O	2.7	2.3	0.5	0.1	0.4	0.4
SO ₃	10.9	2.1	2.4	1.1	23.5	3.1

concentrated along the centerline of the deposit. The trends for silicon concentrations are similar to those of sodium. This similarity may be due to the interaction of sodium with silicates, causing the silicates to be sticky and thus more likely to deposit along the centerline. Changes in aluminum concentration are relatively small; the concentration is essentially constant irrespective of position in the deposit. The calcium concentration changes inversely to the sodium concentration. The highest calcium concentration is at the top of the deposit; in addition, high calcium contents are also noted at the lower outer edges of the deposit. The high concentration of calcium at the top of the deposit is probably due to the presence of a molten phase which traps most of the particles which pass through the constrictor. Iron concentrations are generally higher along the centerline of the deposit.

Tables 27 - 31 summarize the crystalline phases identified in the deposits from some of the Suite 2 coals. The relative abundance of the alkali and alkaline earth aluminosilicates decreases from the top of the deposit to the base. The higher temperature (1200°C) at the top of the deposit promotes the formation of these phases due to increased interaction of the ash constituents during melting. Oxides such as periclase, lime, hematite, spinel, and quartz are commonly found at the base of the deposit. There is also abundant glass material present in the lower sections of the deposits. The crystalline species identified at the base of the deposit are very similar to that of

Table 27. Crystalline phases identified in North Dakota lignite deposits using x-ray diffraction.
(phases listed in order of decreasing abundance)

<u>Deposit Location</u>	<u>Indian Head</u>	<u>Beulah</u>	<u>Velva</u>
Deposit top half	major: melilite pyroxene	major: melilite periclase minor: $\text{Ca}_3\text{Al}_2\text{O}_6$	major: melilite minor: pyroxene
Deposit lower half	major: quartz melilite pyroxene periclase minor: hematite plagioclase	major: melilite periclase minor: $\text{Ca}_3\text{Al}_2\text{O}_6$	major: quartz melilite lime periclase minor: pyroxene hematite trace: anhydrite
Base and white	major: quartz hematite periclase lime minor: Na_2SO_4	major: lime Na_2SO_4 periclase $\text{Ca}_3\text{Al}_2\text{O}_6$ trace: anhydrite	major: quartz lime periclase minor: hematite melilite trace: anhydrite

Table 27. Continued.

<u>Deposit Location</u>	<u>Center(1500°C)*</u>	<u>I/E⁺ Center(1500°C)</u>	<u>Center(1400°C)</u>	<u>I/E Center(1400°C)</u>
Deposit top half	major: pyroxene minor: quartz	major: pyroxene plagioclase minor: quartz melilite	major: melilite pyroxene minor: quartz lime spinel periclase	major: amorphous quartz minor: plagioclase melilite pyroxene hematite
Deposit lower half	major: pyroxene minor: quartz spinel periclase	major: quartz minor: pyroxene plagioclase melilite hematite spinel periclase	major: melilite pyroxene minor: quartz lime spinel periclase	major: amorphous minor: quartz plagioclase trace: pyroxene
Base and white	major: amorphous minor: periclase hematite spinel anhydrite	major: quartz amorphous minor: spinel	major: quartz melilite lime minor: spinel pyroxene trace: anhydrite	major: amorphous minor: quartz trace: hematite spinel

* - Hot zone temperature.

+ - Ion-exchanged.

Table 28. Crystalline phases identified in Gascoyne lignite deposits using x-ray diffraction.
(phases listed in order of decreasing abundance)

<u>Deposit Location</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>
Deposit top half	major: quartz pyroxene amorphous	major: quartz amorphous	major: melilite minor: pyroxene trace: quartz	major: quartz pyroxene
Deposit lower half	major: quartz minor: melilite pyroxene trace: periclase amorphous	major: quartz melilite pyroxene minor: spinel	major: melilite quartz minor: periclase hematite pyroxene	major: quartz melilite minor: periclase pyroxene trace: hematite plagioclase
Base and white	major: quartz minor: periclase melilite lime hematite pyroxene amorphous	major: quartz minor: melilite periclase hematite	major: periclase hematite lime minor: melilite quartz amorphous	major: quartz periclase minor: lime amorphous trace: anhydrite melilite

Table 29. Crystalline phases identified in subbituminous deposits using x-ray diffraction. (phases listed in order of decreasing abundance)

<u>Deposit Location</u>	<u>Dave Johnston</u>	<u>Rosebud</u>	<u>Wyodak</u>	<u>Navajo</u>
Deposit top half	major: quartz amorphous trace: plagioclase melilite	major: quartz minor: melilite plagioclase hematite spinel	major: melilite quartz trace: plagioclase pyroxene spinel hematite periclase	major: quartz mullite
Deposit lower half	major: quartz minor: lime hematite trace: melilite anhydrite	major: quartz minor: plagioclase hematite spinel trace: melilite	major: melilite quartz trace: Ca ₃ Al ₂ O ₆ periclase lime	major: quartz amorphous trace: mullite
Base and white	major: quartz minor: melilite trace: plagioclase hematite spinel	major: quartz periclase trace: melilite hematite lime amorphous	major: lime periclase quartz minor: Ca ₃ Al ₂ O ₆ trace: anhydrite melilite	major: quartz

Table 30. Crystalline phases identified in deposits produced from Rosebud and Rosebud float-sink fractions using x-ray diffraction.
(phases listed in order of decreasing abundance)

<u>Deposit Location</u>	<u>Rosebud</u>	<u>1.4 Float</u>	<u>1.6 Float</u>	<u>1.6 Sink</u>
Deposit top and lower halves	major: quartz minor: plagioclase hematite spinel melilite	major: melilite plagioclase quartz periclase minor: pyroxene	major: quartz plagioclase periclase trace: $\text{Ca}_3\text{Al}_2\text{O}_6$	major: quartz minor: hematite trace: magnetite
Base and white	major: quartz periclase trace: melilite hematite lime	major: periclase quartz minor: amorphous trace: Fe_2O_3	major: periclase quartz trace: Fe_2O_3	major: quartz minor: hematite trace: magnetite

Table 31. Crystalline phases identified in Texas lignite deposits using x-ray diffraction.
(phases listed in order of decreasing abundance)

<u>Deposit Location</u>	<u>San Miguel (1500°C)*</u>	<u>I/E San Miguel (1500°C)</u>	<u>San Miguel (1400°C)</u>	<u>I/E San Miguel (1400°C)</u>	<u>Martin Lake (1500°C)</u>
Deposit top half	major: amorphous	major: amorphous	major: amorphous	major: amorphous	major: plagioclase melilite pyroxene
	minor: quartz	minor: quartz	minor: quartz	minor: quartz	minor: quartz amorphous
Deposit lower half	major: amorphous	major: amorphous	major: amorphous	major: amorphous	major: periclase lime
	minor: quartz	minor: quartz	minor: quartz	minor: quartz	minor: hematite quartz amorphous
Base and white	major: amorphous	major: amorphous	major: amorphous	major: amorphous	major: periclase quartz
	minor: quartz	minor: quartz	minor: quartz	minor: quartz	minor: lime hematite amorphous

* - hot zone temperature.

the fly ash material.

EFFECTS OF FURNACE CONDITIONS ON DEPOSIT FORMATION

Gas Velocity

A test was performed using Upper Hiawatha #1 coal to investigate the extent of deposition and properties of the deposit as affected by furnace parameters such as the gas velocity. The standard gas velocity (3 m/s) was reduced to 0.6 m/s by using a constrictor nozzle with a larger hole (3.18 cm diameter). As shown in Table 32, the amount of the deposit formed from the low gas velocity condition was less than that formed at high gas velocity. The appearance of the deposit was also different. The only formation was a loosely deposited mass covering the entire substrate surface with no sign of fusing in the upper layers. No adherent material was noted after brushing off the loosely deposited material. These experiments demonstrate the influence of gas velocity on the deposit formation process; a drop in gas velocity would result in a decrease in the adhesion force.

Constrictor Angle

In order to reduce direct radiative heat transfer to the deposit, the constrictor nozzle was redesigned with the hole cut at a 60° angle to the horizontal. The deposit amounts are given in Table 33. The typical appearance of the deposit for the three

Table 32. Deposit mass and percent ash recovered as deposit for
test coals: total coal feed - 10 g; feed time = 30 min.

Coal	ASTM ash, wt.% [*]	Height of deposit, cm	Deposit mass, mg	Ash recovered as deposit, %
<u>Normal constrictor (1.27 cm dia.)^a</u>				
U.Hiawatha #1	9.4	1.4	568	60
<u>Normal constrictor (3.18 cm dia.)^b</u>				
U.Hiawatha #1	9.4	0.3	424	45

Table 33. Deposit mass and percent ash recovered as deposit for
test coals: total coal feed = 10 g; feed time = 30 min.

Cal	ASTM ash, wt. %	Height of Deposit deposit, cm	mass, mg	Ash recovered as deposit, %
<u>Normal constrictor (1.27 cm dia.)^a</u>				
U.Hiawatha #1	9.4	1.4	568	60
Powder River Basin	4.6	1.0	320	65
N.Dakota	7.1	1.3	367	52
<u>60° angled constrictor (1.27 cm dia.)^a</u>				
U.Hiawatha #1	9.4	1.9	380	40
Powder River Basin	4.6	2.0	223	49
N.Dakota	7.1	2.0	202	29

coals tested with this arrangement is shown in Figure 18. As the deposit grows it bends the gas path to pass across the substrate disk, thus leading to deposition of larger particles in the "elbow" of the deposit, with smaller particles at the opposite side of the deposit.

Sodium sulfate crystals were found on the opposite side of the substrate from the deposit mass after tests with Upper Hiawatha #1 and the North Dakota lignite. To confirm the possibility of sodium sulfate crystals depositing under these conditions, sodium sulfate powder (-38 micron) was passed through the furnace under otherwise similar experimental conditions. Crystal shapes and energy-dispersive x-ray fluorescence spectra of the deposit produced from sodium sulfate were similar to those for the deposits from the coals. The dust produced from the Powder River Basin coal contained a mass of needle-shaped crystals. The EDS of different areas of the dust indicated either calcium sulfate or a combination of sodium and calcium sulfates. Large, deformed particles of calcium sulfate were found in the elbows of the deposits from North Dakota lignite and Powder River Basin coal.

Hot Zone Temperature

The effect of hot-zone temperature was determined in tests with Suite 2 coals. Center (North Dakota) and San Miguel (Texas) lignites were tested with hot zone temperatures of 1400 and

Figure 18. Appearance of deposit from N. Dakota lignite
(60° angled constrictor).

1500°C. There is a marked difference between the two temperatures in the amount of fused material in the deposit and in the crystalline phases present. San Miguel has a similar behavior. Pyroxene is the major crystalline species in the top of the Center deposit formed with a hot zone temperature of 1500°, but melilite is more abundant than pyroxene in the deposit from the 1400° test.

Further tests were done to determine the effects of first removing the ion-exchangeable cations from these two lignites and then comparing the two hot zone temperatures. For the Center lignite there was no appreciable difference in the deposit weight for tests at the two hot zone temperatures. However, for the San Miguel lignite a significant reduction in sticking fraction (the weight of deposit divided by the weight of ash in the coal fed to the furnace) was observed at the lower temperature. The difference in observed behavior of these two lignites and their ion-exchanged counterparts is likely attributable to the differences in the modes of incorporation of the inorganic constituents. This point is discussed in more detail later, in the subsection dealing with the growth of the deposit.

PHYSICS AND CHEMISTRY OF FLY ASH SINTERING

This section discusses the thermophysical changes-development of strength and shrinkage - and the chemical changes occurring during fly ash sintering. The experiments described in this section were performed in a special sintering furnace, to be described below, and not in the drop-tube furnace. This work therefore represents a collateral line of investigation to the main thrust of the combustion studies. However, an understanding of the sintering process is important for understanding the development of strength in the slag deposits, a phenomenon to be described in the following section. For that reason we digress from the discussion of combustion conditions and deposit formation to interject the results of fundamental studies of sintering studies, to set the stage for some of the later discussion of mechanisms of deposit formation.

The sintering of ash is an important part of the overall deposition process. Tests were performed in the present study for the specific purpose of evaluating the sintering characteristics of ash. The approach was to sinter fly ash pellets at various temperatures, times, and atmospheres to simulate the conditions at different locations within the deposit. After sintering, the sinter strength and extent of shrinkage were measured and chemical changes were monitored by x-ray diffraction.

Soda-lime-silica glass (soda glass) is a homogeneous material which has been used as a model to study viscous flow sintering near 600°C.^{3,4,5,6} On the other hand, fly ash, in particular that from high-rank coals, is a heterogeneous material composed of low melting point components (glass) and high melting point components (crystalline materials). As a consequence, pure soda glass alone may not be a suitable model for comparison with the sintering of fly ash. A mixture of soda glass and alumina may more closely simulate a fly ash system. The soda glass used in this study had a composition of 75% SiO₂, 8% CaO, and 17% Na₂O.

Sintering studies were conducted in a dedicated test system, shown in Figure 19. The furnace uses electrical resistance heating to attain a maximum temperature of 1300°C with a rate of 6-8° per minute. The heating element is a platinum - 40% rhodium wire heated by a 120 volt, 10 amp variable power supply. The sample temperature was measured using a Type S thermocouple (platinum / platinum-10% rhodium) attached to the sample crucible.

To determine the sinter point, the material to be tested was loosely packed (750 kg/m³) into a 10 mm diameter, 25 mm high crucible. A 10 mm diameter, 0.5 mm thick disk of platinum foil was used as an electrode by placing it in the bottom of the sample crucible making contact with another platinum foil disk beneath the crucible, as part of an electrical circuit to measure the ash resistance. The platinum electrodes were connected to a

Figure 19. Ash sintering furnace.

15 volt stabilized DC source. A 15 - 10,000 ohm variable resistor was placed in one of the leads, and a potentiometric recorder was connected across the resistor. The ash resistance is related to the variable resistor setting and the voltage drop, as measured by a recorder, as a function of temperature. A plot of log resistance (R) versus $1/T$ (absolute) normally gives a straight line, the slope of which changes as sintering commences. The temperature at the point of change in slope is called the electrical sinter point.

The Barnhart and Williams compressive strength test⁷ was modified by preparing an ash pellet having a bulk density comparable to that of the deposit in a boiler and using the conditions under which sintering in the radiant section takes place. To determine the compressive strength, a green pellet was made from 0.12g of ash mixed with a drop of distilled water and compressed in a die at pressures sufficient to give a 5 mm diameter, 5mm high cylinder having a bulk density of 1200 kg/m³. The pellet was put in a 10 mm diameter, 25 mm high alumina crucible which was heated in the sintering furnace at 6-8°/min in air to the desired temperature and held at temperature for the desired time period. The pellet was allowed to cool to room temperature inside the furnace; cooling required approximately three hours. The diameter of the cold pellet was measured. The compressive strength determination was performed using an Instron apparatus.

The compressive strength of the sintered ash pellet can be measured at room temperature after removal of the cold sintered pellet from the furnace or at high temperature by placing the furnace in the Instron apparatus. To determine strength at room temperature, the sintered pellet was placed on a flat 3 x 4 x 0.5 inch stainless steel plate in the apparatus and crushed by raising it vertically against the load cell attachment. The output of the load cell was read from a potentiometer. The compressive strength at high temperatures can be determined by placing the furnace assembly in the Instron apparatus. By raising the furnace in the apparatus against the stationary alumina rod and load cell attachment, the load reading was then obtained. For tests performed in a reducing atmosphere, a 45% CO, 20%CO₂, 35% H₂ mixture was introduced and removed through the alumina tube assembly. The other exits were sealed with high temperature fiber packing to prevent gas from leaking into the furnace. The gas flow was controlled at 400 cm³/min.

The sinter point of pure soda glass was 525°C. The alumina, which has a melting point of 2045°, gave a sinter point greater than 1200°. The mixture of soda glass and alumina exhibited a sinter point at 550°. This result indicates that the properties of soda glass are a determining factor in the sintering process. There was no development of strength in the heat treatment of alumina up to the maximum test temperature of 1200°, whereas strength development of the soda glass - alumina mixture began at 800° and showed a small increase with temperature. This

observation suggests that soda glass, which is the low melting point component, initiates and enables viscous flow sintering to occur at the low temperatures.

The effect of time on sintering was carried out using fly ashes from Upper Freeport and Beulah coals. The size distribution, ash fusion temperatures, spectrochemical, and mineralogical analyses of these ashes are given in Tables 34-37.

The Upper Freeport pellets heated below the sinter point ($<800^{\circ}$) did not develop strength, even after holding at the test temperature for several hours. No shrinkage was observed. The pellet remained as a loose powder when removed from the furnace, indicating that no sintering had occurred. The strength of the Upper Freeport pellets heated at 950° and 1000° (above the sinter point) increased with time from 15 minutes to 25 hours. As the heat treatment temperature increased to 1000° the slope of the compressive strength vs. time curve increased, showing that the rate of sintering increased with temperature. When the pellets were heated at even higher temperatures ($1050 - 1150^{\circ}$), a maximum in strength was noted. The higher the heat treatment temperature, the shorter the time needed for developing the maximum strength. For example, the maximum strength was developed in one hour at 1050° , as compared to 15 minutes at 1150° .

The Beulah fly ash had a sinter point of 550°C . The strength

Table 34. Size distributions (Microtrac) of test materials: fly ash

Material	U.Freeport	Montour	Ill. #6	Illinois#6 gasifier ash	Beulah	Water-washed U.Freeport	HF-washed U.Freeport
Size (μm)	Cumulative wt.% less than size						
44	100.0	100.0	100.0	100.0	100.0	100.0	100.0
31	100.0	100.0	100.0	96.1	100.0	100.0	100.0
22	100.0	100.0	100.0	89.1	80.6	100.0	96.8
16	100.0	100.0	95.0	79.5	65.0	100.0	91.4
11	95.2	84.3	72.2	68.2	52.4	96.9	83.9
7.8	78.2	71.0	54.8	56.5	42.2	76.2	74.8
5.5	64.3	59.9	41.7	45.5	34.0	59.9	64.9
3.9	52.8	50.5	31.7	35.7	27.4	47.1	54.9
2.8	43.6	42.6	24.0	27.6	22.1	37.0	45.5
2.0	35.5	35.9	18.3	21.0	17.8	29.1	37.1
1.4	29.3	30.2	13.9	15.8	14.4	22.9	29.8
1.0	24.0	25.5	10.6	11.8	11.6	18.0	23.7

Table 35. Size distributions (Microtrac) of test materials and additives.

Material	U.Freeport min. mix.	Fused U.Freeport min. mix.	Iron silicate	Calcium silicate	Pyrite	Alumina powder
Size (μm)	Cumulative wt.% less than size					
44	100.0	100.0	100.0	100.0	100.0	100.0
31	100.0	88.7	100.0	100.0	100.0	100.0
22	100.0	74.5	95.3	90.9	93.7	100.0
16	94.5	62.8	89.8	82.4	86.9	100.0
11	73.5	52.8	83.7	74.4	79.9	70.7
7.8	57.1	44.4	77.1	67.0	72.9	50.0
5.5	44.4	37.3	70.4	60.1	65.9	35.4
3.9	34.5	31.4	63.7	53.9	59.2	25.0
2.8	26.9	26.4	57.1	48.1	52.8	17.7
2.0	21.1	22.2	50.8	42.9	46.9	12.5
1.4	16.2	18.7	45.0	38.2	41.4	8.8
1.0	12.6	15.7	39.5	33.9	36.4	6.3

Table 36. Fusion temperature($^{\circ}\text{C}$) of test materials.

	U.Freeport			Montour	Ill. #6		Beulah	Synthetic	Soda glass	Soda glass: alumina (1:1)
	ASTM [*] ash	Fly ash	HF-washed	ASTM [*] ash	ASTM [*] ash	Fly ash	Fly ash	Min. mix.		
<u>Oxidizing atmosphere</u>										
Initial deformation	1390	1410	1420	1430	1280	1220	1200	1370	890	1340
Softening	1420	1480	1450	1450	1300	1250	1220	1390	900	1370
Hemisphere	1450	1520	1460	1470	1350	1280	1230	1420	1160	1410
Fluid	1480	1520	1500	1480	1370	1290	1260	1460	1260	1460
<u>Reducing atmosphere</u>										
Initial deformation	1200	1400	1400	1240	1090	1110	1070	1290	920	1280
Softening	1350	1440	1440	1320	1120	1140	1080	1400	950	1340
Hemisphere	1420	1480	1470	1360	1140	1180	1100	1420	1090	1410
Fluid	1480	1520	1480	1420	1180	1220	1140	1460	1270	1460

* high temperature ASTM ash.

Table 37. Spectrochemical analysis of test materials.*

	U. Freeport fly ash	Montour fly ash	Illinois #6 fly ash	Illinois #6 gasifier fly ash	Beulah fly ash	HF-washed U. Freeport fly ash	U. Freeport synthetic mineral mixture
Weight percent of equivalent oxides							
SiO ₂	53.5	51.1	44.7	46.5	28.8	34.9	58.0
Al ₂ O ₃	28.2	27.7	19.7	20.3	14.8	42.7	24.8
TiO ₂	1.4	1.3	1.0	1.0	0.6	2.9	0.0
Fe ₂ O ₃	6.3	10.5	15.7	16.0	14.6	14.1	11.6
MgO	1.3	1.4	1.9	1.9	6.2	0.5	0.0
CaO	3.1	2.3	5.1	5.2	20.4	0.1	0.8
MnO	0.0	0.0	0.1	0.1	0.1	0.0	0.0
SrO	0.0	0.0	0.1	0.0	0.7	0.0	0.0
BaO	0.0	0.0	0.1	0.1	0.9	0.1	0.0
Na ₂ O	0.4	0.3	0.9	0.9	9.0	0.1	0.0
K ₂ O	2.9	2.8	1.9	2.0	0.6	0.2	4.8
P ₂ O ₅	0.5	0.6	0.5	0.0	0.3	0.0	0.0
ZnO	0.0	0.0	0.6	0.0	0.0	0.5	0.0
SO ₃	0.9	1.5	6.2	5.6	3.1	0.2	---
Total	98.0	98.0	98.2	100.0	100.0	95.8	100.0

*Source = Mineral Constitution Laboratory, The Pennsylvania State University, Pa.

of pellets heat treated at 950° to 1050° showed no significant increase and no shrinkage with time. At 1150°, however, the strength of pellets increased with time and the pellets underwent some shrinkage. No maximum was noted in the strength of the Beulah fly ash, in contrast to the Upper Freeport ash. Presumably different sintering mechanisms were involved. The results of these tests suggest that the sintering time affects the sintering behavior, which in turn is dependent upon the heat treatment temperature and type of ash. The fly ash from high rank coal shows a greater effect than that from low-rank coal.

These tests showed that appreciable strength was achieved in a one hour heat treatment time in most cases. Thus one hour was chosen as a standard sintering time in subsequent tests to evaluate sintering as a function of temperature.

Compressive strength tests performed at room temperature on Upper Freeport fly ash sintered at 1150°C for one hour in air indicated linear stress with applied linear strain up to about 10% strain, followed by brittle fracture with a sudden large decrease of stress. At 700° the failure strength was essentially the same, but there appeared to be enough ductility to require a higher strain to give failure. The fracture also was less explosive, so that the fall in stress as strain increased was less abrupt. At the heat treatment temperature of 1150°, the pellet deformed steadily to high strain, leading to a flattened pellet. This is clear evidence for the presence of a viscous

liquid phase at temperatures above the sinter point. This viscous liquid phase became solid at temperatures below the sinter point, causing no difference in the results of compressive strength between the test below the sinter point and the room temperature test. At the temperatures below the sinter point, solidification of the liquid phase and extensive sintered bond formation result in a strong pellet. In a boiler, as a deposit continues to build up, the temperatures of the inner deposit layer can cool to the extent that solidification of a viscous liquid phase can occur. The sootblowers may then be ineffective in removing the strong deposit.

Further studies also incorporated Montour and Illinois #6 fly ashes; data on these ashes has been tabulated previously. The sinter points of Upper Freeport and Montour fly ash were identical (800°C), whereas Illinois #6 fly ash was slightly lower at 725°. Beulah fly ash showed by far the lowest sinter point at 550°. Strength development in the Beulah ash began at 400° above the sinter point. X-ray diffraction analysis showed significant amounts of sodium and mixed alkali sulfates in the Beulah fly ash. These phases have low melting points that would give liquid ionic conduction at low temperatures and cause a change in the slope of $\log R$ vs $1/T$. It is likely that the change in slope is not due to changes in particle geometry (e.g., growth of sinter necks), but due to the normal presence of a liquid phase formed at the sinter point. Fly ashes from high rank coals contain only traces of the alkali and mixed alkali sulfate phases, so higher

temperatures were required to generate the liquid phase and cause a change in the slope of the plot. These fly ashes started to develop strength at about 100 - 200° above their sinter points.

Upper Freeport, Montour, and Illinois #6 fly ashes showed a maximum in strength development as a function of heat treatment temperature. The maximum in strength corresponded to a maximum in shrinkage of the ash pellet. At heat treatment temperatures above that at which the maximum strength was developed, the shrinkage was not as great as it was at the temperature of maximum strength. Beulah fly ash showed a small increase in strength with temperature. No dimensional change was observed in Beulah fly ash pellets except for the pellet heat treated at 1150°.

SEM examination of Upper Freeport sintered pellets clearly indicated the development of sinter necks and the formation of a glassy phase. The maximum strength appears to be related to the greatest glass content in the pellet. X-ray diffraction analysis showed significant amounts of glass plus crystalline material such as quartz, hematite, and mullite. A postulated mechanism for the rise and subsequent fall of strength vs. temperature is as follows: At the temperature at which strength development begins (about 850°C for Upper Freeport), the low melting glass material originally present in the fly ash formed a liquid phase, enabling viscous flow sintering to occur. As the heat treatment temperature increased, the viscosity of the liquid decreased. In addition, the total amount of liquid probably increased from

melting of higher melting point glass material and by dissolution of other high melting point components into the liquid phase. This resulted in the shrinkage of particles, followed by the growth of the larger ones, producing a structure of coalescence of round grains surrounded by a liquid, shown in Figure 20. Shrinkage and sintering at this stage proceeded rapidly because of the presence of sufficient liquid phase to fill the pores and because of the high mass transfer diffusion coefficient in a liquid. The resulting matrix had a very high strength because the liquid phase produced a glass upon cooling and gave associated sintered bond formation in the heat treated pellet. The decrease in strength and reversal of shrinkage at the higher heat treatment temperatures (above 1050° for Upper Freeport) was associated with the formation of crystalline phases, particularly mullite. The content of crystalline phase appears to increase with temperature and a gradual decrease in glass content was observed. The formation of mullite could be a result of the thermal decomposition of the aluminosilicate glass, implying that some of the bonding glass was removed from the sintering mass. Since mullite has a melting point of 1810°C, any mullite formed during sintering would remain as a crystalline solid at the heat treatment temperatures of 900 - 1200°. The reduction in strength at high temperatures is thus due to the reduction of the bonding glass phase by transformation of the glass into a crystalline phase. This transformation raises the viscosity of the residual liquid and hence reduces the rate of sintering.

Figure 20. SEM photomicrographs of the structure of cold pellets from U. Freeport fly ash, as a function of heat treatment temperature for 1 hour in air; (a) as received fly ash (after burning off carbon); (b) sintered at 950 $^{\circ}\text{C}$; (c) sintered at 1050 $^{\circ}\text{C}$; and (d) sintered at 1200 $^{\circ}\text{C}$.

Montour fly ash developed higher strength than Upper Freeport in the temperature range of 850 - 1000°C. A greater glass phase content was observed in the x-ray diffraction pattern of the Montour sintered pellet, compared to that of Upper Freeport, at 1000°. The high glass content in the Montour ash would indicate that large amounts of liquid phase formed. Sufficient liquid would bring most of the particles together and fill most of the pores, causing sintering to take place rapidly. The formation of crystalline phases - anorthite and mullite - in the Montour pellet again appears to correspond to the reduction in strength at high temperatures (>1000°). The comparative sintering behavior of Upper Freeport and Montour fly ash is in accord with the utility experience using these two coals, since the Montour coal gives less problems with upper furnace soot-blowing operation than Upper Freeport coal.

Fly ash from Illinois #6 coal showed the same characteristic rise and fall of strength with temperature but gave the lowest maximum strength of any of the high-rank coal fly ashes tested. A significant amount of crystalline phase formation occurred at temperatures as low as 1000°C, probably due to the relatively high content of calcium in this ash, which would readily interact with the glassy aluminosilicate phase to form crystalline anorthite. The formation of anorthite would readily remove the bonding glass and reduce the strength of the pellets. In this case the development of mullite crystals above 1050° was not observed, suggesting that the bonding phase was largely removed

by forming anorthite.

It is concluded from these observations that there probably exists two viscous flow mechanisms in the sintering of fly ashes from high-rank coals, one with a reactive liquid phase at low temperatures (850 - 1050°C) and one with a non-reactive liquid phase at higher temperatures (1050 - 1200°). As a result, the rise and fall of strength with temperature is a sintering characteristic of the fly ashes from high-rank coals.

The sintering characteristics of Beulah lignite fly ash exhibited a behavior different from those of the fly ashes from high-rank coals. Only a small increase in strength with temperature was observed. No maximum strength and no shrinkage occurred until the heat treatment temperature of 1150°. Crystalline phases in the sintered products were predominant over the glass material. The crystalline phases that formed at 950° include the melilite series of minerals: gehlenite ($\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7$), sodium melilite ($\text{NaCaAlSi}_2\text{O}_7$) and nepheline (NaAlSiO_4). As the heat treatment temperature increased, the x-ray diffraction peaks of the melilites increased in intensity. In addition, the sodalite minerals hauyne $(\text{Na,Ca})_{4-8}(\text{Al}_{12}\text{Si}_{12}\text{O}_{24})(\text{SO}_4)_2$ and nosean $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{SO}_4$ were identified. Significant amounts of glass and alkali sulfates were detected in the as-received fly ash. These materials would, in principle, provide a liquid phase enabling sintering to occur. However, some of the liquid formed at the heat treatment temperature may have been quickly removed

by interactions of the abundant alkali and alkaline earth sulfates and aluminosilicate glass to form crystalline phases. Thus the strength of pellets resulted mainly from the properties of the newly formed crystalline phases, i.e., from the formation of crystalline bridges between particles. These observations suggest that the sintering of fly ash from low-rank coals displays a viscous flow with non-reactive liquid phase mechanism under these conditions (850 - 1150°).

Melilites and sodalites have been found in the deposits formed in boilers firing high-sodium low-rank coals.^{8,9} It is thought that the strength resulting from the crystalline properties of these materials makes bonded deposits in boilers difficult to remove on-load. The results from this study are in accord with this earlier work. However, the observed sintering behavior of the Beulah fly ash under the conditions used in this investigation may not perfectly simulate the actual sintering behavior of bonded deposits in boilers. In boilers there is a constant stream of alkali and sulfur oxide vapors in the flue gases which pass through the bonded deposit. These vapors could develop sufficient liquid phases from sodium and mixed alkali sulfates, sodium melilite and sodalites in the deposit matrix to enhance the sintering rate and make the bonded deposit stronger and harder than observed in this investigation.

In terms of analyzing the sintering process it is important to discern whether the formation of a liquid phase during

sintering occurs from melting of some of the fly ash spheres, or is due to the surface of most spheres becoming liquid due to surface fluxing. Figure 21 shows the appearance of Upper Freeport fly ash washed with 10% hydrofluoric acid solution. The surfaces of the particles were etched, revealing the roughness of crystalline skeletons (probably mullite). The HF-washed ash did not develop appreciable strength or show shrinkage below 1150°. The lack of glass material on the surfaces of the HF-washed spheres and the resulting production of a weak deposit indicated that sintering occurs at the surface of most fly ash spheres.

The addition of calcium sulfate to the Upper Freeport fly ash reduced the strength of the sintered deposit. At 950°C a significant amount of calcium sulfate was detected by x-ray diffraction, indicating that the calcium sulfate did not decompose and had no effect on the sintering behavior of the fly ash. However, at 1000° the intensity of the calcium sulfate peaks started to decrease and anorthite was detected, showing a reaction with the aluminosilicate glass to produce anorthite. As the temperature increases, calcium sulfate and quartz disappeared, whereas anorthite increased. These phenomena appeared to be associated with the reduction in strength. The reaction between calcium sulfate and ash has been studied by thermogravimetric analysis.¹⁰ In a 1:1 calcium sulfate/ash mixture a weight loss was observed at 1000° whereas calcium sulfate alone showed signs of weight loss only above 1300°. The temperature at which the calcium additive reacts with ash

Figure 21. SEM photomicrographs for the structure of cold pellets from HF-washed U. Freeport fly ash; (a) as received HF-washed fly ash; (b) sintered at 950 °C for 1 hour in air; (c) sintered at 1100 °C for 1 hour in air; and (d) sintered at 1150 °C for 1 hour in air.

components to reduce strength agrees with the thermogravimetric observations. It is also interesting to note that calcium carbonate has been shown to be an effective additive for reducing deposit strength in a full-scale boiler.¹¹

The foregoing evidence suggests that changes in quantity, viscosity, and composition of the glassy phase during sintering lead to changes in the rate of sintering. Therefore, either removing the glass material from the fly ash or increasing the crystalline phase in the matrix by using an additive could minimize the strength of sintered deposits formed in boilers. The laboratory method developed in this study could be used to determine the optimum additives and conditions of sintering. The appropriate additive and conditions could then be tested in an actual boiler to effectively reduce the deposit strength.

PROPOSED MECHANISM OF DEPOSIT FORMATION

The formation of an ash or slag deposit on the heat transfer surfaces of a pulverized coal fired boiler can be explained by the following sequence of events:

1. Fly ash formation in the combustion zone and subsequent transportation of fly ash toward the heat transfer surfaces.
2. Initial adhesion of the ash particles onto the heat transfer surfaces.
3. Continued build-up of the deposit on the initial layer of adherent ash particles (the sticking process).
4. Interactions between the deposited ash particles to form a strong deposit matrix (the sintering process).

The findings of this project relevant to each of these events are presented and discussed in the sections which follow.

Formation and Transportation of Ash Particles

The transport of the ash particles from the high temperature gases onto the heat exchange surfaces either by inertial impaction or by diffusion. The factors determining which of these mechanisms is predominant are the size and mass of the ash particles, the flue gas velocity, and the aerodynamic conditions around the heat exchange surfaces.¹² Large ash particles have a sufficiently large kinetic energy to leave the streamlines and

impact on the surfaces they encounter. These impacting particles have an increased probability of adhesion because the kinetic energy of the particle is transformed to heat upon impact, possibly causing, or increasing the extent of, partial melting enough to increase the sticking behavior of the particle. The small ash particles or inorganic vapors move toward the surfaces by Brownian motion, by turbulent diffusion, or by thermophoretic diffusion through the temperature gradient in the boundary layer.

The upper part of the furnace is exposed to lower flue gas temperature than the lower part of the furnace. The ash droplets have cooled sufficiently so that they might be expected not to deposit in this region. However, upper wall slags are known to exist and have been found to be enriched in certain fractions of the ash. The mechanism of formation of upper wall slag appears to be the selective deposition of specific inorganic species. Presumably the origin of these species is the result of the presence of low melting inorganic components of composition differing from the mean ash composition. Pilot-scale combustion of high rank bituminous coals showed that the deposition of iron-rich ash particles in the upper wall regions occurs mainly by the inertial impaction process.¹³

Adhesion of Ash Particles on Heat Exchange Surfaces

The transport of ash particles to the heat exchange surfaces is not by itself sufficient to cause deposit formation if the

particles are not retained on the surface after collision. The nature of the particle - surface interaction is determined by the physical and chemical properties of the ash particles and of the surface, the temperature, and the conditions of gas flow around or over the surface. The prime mode of deposition of the adherent particles is by inertial impaction. All other factors being equal, sticky or molten particles adhere more readily than solid particles. In a large pulverized coal fired boiler, supercooling of a molten ash droplet may occur due to a rapid cooling below its melting point without the formation of a solid phase. A similar process may also occur on the surfaces of ash particles, forming a viscous, sticky surface glaze that can adhere and strongly bond to the boiler tube surfaces or stick to already adhered ash particles to form a strong deposit.

A coal with a low ash fusion temperature can be expected to give ash deposition problems. The ash fusion test (ASTM D-1857) has been used to provide a warning to boiler designers and operators about such coals. If ash particles arrive at heat exchange surfaces at a temperature below their fusion temperature, they will not form a bonded structure but instead will settle out as dust. Removal of these deposits by sootblowing is comparatively simple. On the other hand, if ash particles arrive at a heat transfer surface at a temperature at or higher than the fusion temperature, they will be very sticky and the resulting deposit will be tightly bonded, hard, and difficult to remove.

The formation of a bond between an ash particle and boiler steel surfaces depends upon the composition and thermal behavior of the oxide layer on the steel. If the chemical composition of the ash particle is compatible with the oxide layer and the thermal properties are similar, the possibility of forming a strong bond is great. In addition, the surface tension and wetting ability of the particle when it reaches the steel surface influences its ability to flow across the steel, allowing interaction of the ash particle with the oxide layer. As will be discussed in detail below, the particles with the greatest strength of adhesion were rich in iron and silicon or iron and sulfur. Iron-containing silicates are known to wet readily most surfaces except carbon.¹⁴ The ternary phase diagram of the $\text{FeO-SiO}_2\text{-Al}_2\text{O}_3$ system¹⁵ indicates a low melting point region of 1200°C , which is lower than the temperature of the gases passing through the constrictor. The phase diagram of FeO-FeS ¹⁴ indicates a eutectic melting as low as 930°C ; particles of this eutectic composition would likely be molten when the particle impacted the boiler steel surface.

Burner and wall slags occur in the lower part of the furnace where the metal temperatures of the waterwall tubes are the lowest. The lower part of the furnace around the flame is exposed to the highest rate of heat transfer and the hottest part of the flame, which will bring molten ash particles to the wall as liquid droplets. Drops of molten ash will not readily stick to

the cool surface in this region unless the composition of the drops is rich in iron (from decomposition of pyrite), a characteristic which gives sticking and slag initiation at relatively low metal temperatures.¹

Examination of the microstructure of a boiler wall slag with an electron microscope and microprobe showed that the slag region adjacent to the furnace wall consisted primarily of a glassy phase layer having high porosity, and that the slag region near the flame side contained a high proportion of crystalline phases and less porosity.¹⁶ The high proportion of glassy material next to the tube indicates that the first formed slag layer has been cooled rapidly to a temperature at which crystallization is insignificant.

In previous work studying the adhesion behavior of coal ashes on heat exchanger materials, it was postulated that it was necessary for the surface to have an oxide layer in order for adherence to occur.¹ However, it was not conclusively shown that the bonding of the drop to the surface was via a chemical interaction, since alternative mechanisms might apply. It is known that the oxidation of a boiler steel in air produces an oxide layer with microporosity, and it is possible that flow of liquid material from the slag drop into these pores causes a mechanical anchoring after the drop has frozen. To test this alternative mechanism, an investigation of slag adherence on a reduced steel surface with high microporosity was conducted under

a reducing atmosphere (45% CO, 25% CO₂, and 35% H₂).

The sticking test was developed specifically to study those factors which influence the adhesion or non-adhesion of a drop of molten ash to a metallic substrate.¹⁷ The test consists of forming a 2 mm diameter x 2 mm high pellet of powdered material around a small hook in the end of a 0.2 mm diameter platinum wire. The pellet is heated in the center of the three nozzle ring burner system shown in Figure 22. The flame is a methane - oxygen flame whose temperature can be varied by changing the relative flow rates of the methane and oxygen. As the pellet is heated it melts; when the viscosity is low enough a molten droplet falls off the wire. The droplet falls about 5 cm through the hole in the cap to the test substrate. (The cap shields the substrate from radiation from the flame, and enables the temperature of the substrate to be controlled accurately by an auxiliary electric furnace and small platinum heater.) The drop freezes on the substrate. The apparent contact angle is measured, and then the drop is sheared off the hot substrate by a ram connected to a force measurement system (shown in Figure 23). The test is repeated with identical pellets at increasing steps of substrate temperature.

The sticking test technique was previously tested on four coal ashes (prepared by the standard ASTM ashing procedure) using a methane - oxygen flame with an adiabatic flame temperature of 1750° C and a pre-oxidized mild steel substrate.^{18,19} It was

TOP VIEW OF RING BURNER

SIDE VIEW OF STICKING APPARATUS

Figure 22. The sticking apparatus: diagram.

Figure 23. Device for measuring adhesion force.

found that the drop would not adhere when the substrate temperature was below a critical temperature, called the sticking temperature. The sticking temperature was typically 425 - 500° C, which is similar to the temperature of boiler wall tubes. Above this temperature, the adhesion strength increased roughly logarithmically with increasing substrate temperature. Although the behavior of the ash melted as a whole may not be a sufficient guide for the formation of slag deposits, the previous work did demonstrate a roughly quantitative method for the study of adhesion.²⁰

The sticking test procedure used in this investigation involved forming a pellet from low temperature ash (LTA ash), or from pure minerals or mineral mixtures ground to -38 microns. Ash or mineral pellets are made from a paste formed by mixing about 5 grams of the ash or minerals with a drop of distilled water and two drops of 10% polyvinyl alcohol solution, and then drying at 110° C for one hour.

The substrate is a rectangular steel piece 35 x 19 x 6 mm. A hole for a thermocouple (Pt / 10% Pt-Rh) is drilled into the end of the substrate close to the upper surface. The thermocouple is held in place by being cast in alumina cement. The pretreatment conditions were as follows: The substrates were first wet polished with 240, 360, 400, and 600 grit silicon carbide papers. For tests under oxidizing conditions, the substrates were oxidized at 400° C for 20 hours in air. The investigation of slag

adhesion on a reduced steel surface required a special pretreatment of the substrate: After the air oxidation just described, the substrate was then placed in the holder of the sticking apparatus and reduced with a flow of reducing gas mixture (35% H_2 , 45% CO , and 20% CO_2) at $500^\circ C$ for 72 hours.

The flame used to melt the pellet was fuel rich with a temperature of about $1600^\circ C$ (measured by an optical pyrometer). The suspended pellet was held in the middle of the flame zone of the three nozzle ring burner until it melted and fell onto the substrate maintained at constant temperature. The adhesion force was measured by tilting the sticking furnace 90° to determine whether the ash drop adhered under the force of gravity. If the ash drop stuck, the adhesion force was measured by bringing the ram of the adhesion force apparatus into contact with the drop and raising the ram until shear occurred.

The proximate and ultimate analyses, the analyses of the ASTM ash, the mineralogical analysis of the LTA, and the ash fusion temperature of the ASTM ash are given for the three tested coals in Tables 38, 39, 40, and 41, respectively.

Figure 24 shows SEM photomicrographs of the interface between an Illinois #6 LTA drop adhered to an oxidized type T-11 steel substrate in air. The drop wetted the oxide layer on the steel, giving a smooth interface between the drop and the steel. However, cooling to room temperature cracked the oxide layer from

Table 38. Proximate and ultimate analyses* of test coals.

Coal	Pittsburgh #8	Illinois #6	U.Hiawatha #1
Moisture	2.00%	6.83%	6.36%
<u>Proximate analysis (dry basis), wt.%</u>			
Vol. matter	37.52	34.28	40.32
Ash	10.02	22.32	11.49
Fixed carbon	52.46	43.40	48.19
<u>Ultimate analysis (dry basis), wt.%</u>			
Nitrogen	1.29	0.86	0.85
Carbon	72.80	58.10	69.70
Sulfur	2.00	4.96	0.45
Oxygen (diff.)	9.38	10.01	13.41
Ash	10.02	22.32	11.49

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, PA.

Table 39. Chemical composition of ash of test coals: expressed as wt.% oxides in high temperature ash (ASTM)*.

Coal	Pittsburgh #8	Illinois #6	U.Hiawatha #1
HTA wt.%	9.9	19.7	10.9
SiO ₂	51.1	48.3	51.1
Al ₂ O ₃	26.9	17.5	13.4
TiO ₂	0.9	0.8	0.9
Fe ₂ O ₃	15.2	20.9	6.2
CaO	0.9	4.7	14.1
MgO	0.6	0.9	2.2
Na ₂ O	0.2	0.6	2.1
K ₂ O	2.2	1.6	0.8
P ₂ O ₅	0.1	0.2	0.3
SO ₃	0.7	4.6	8.3

* Source = Mineral Constitution Laboratories, The Pennsylvania State University, PA.

Table 40. Mineralogical analysis⁺ of LTA from test coals. [@]

Coal	Weight %		
	Pittsburgh #8	Illinois #6	U.Hiawatha #1
LTA	11.8	22.0	12.1
Minerals			
quartz	23	25	28
pyrite	27	29	2-5
kaolinite	25	5	9
illite + mixed layer clays	10*	35*	30*
calcite	n.d.	2-5	7
ankerite	n.d.	n.d.	2-5
unidentified	n.d.	n.d.	10-15*

* estimated value; n.d. = not detected.

+ Source = Mineral Constitution Laboratories, The Pennsylvania State University, PA.

[@] low temperature ash.

Table 41. Fusion temperature of HTA ash, °C from test coals. [@]

Coal	Pittsburgh #8	Illinois #6	U.Hiawatha #1
<u>Oxidizing atmosphere</u>			
Initial			
deformation	1280	1430	1170
Softening	1300	1460	1180
Hemisphere	1350	1470	1220
Fluid	1370	1490	1310
<u>Reducing atmosphere</u>			
Initial			
deformation	1090	1310	1120
Softening	1120	1330	1150
Hemisphere	1140	1370	1180
Fluid	1180	1420	1220

[@] high temperature ash (ASTM).

(a)

(b)

Figure 24. SEM photomicrographs showing cross-section characteristic of interface between Illinois #6 LTA drop and oxidized T-11 steel substrate. Magnification of (b) fifty times that of (a).

the steel. The drop cracked at the interface, demonstrating the high thermal stresses produced on cooling to room temperature. Figure 25 illustrates the results of an automated SEM-EDS analysis across the interface, indicating the gradual change in composition across the interface. Figure 26 shows the interface between the oxide layer and the drop. Figure 27 shows an iron map, with a low density of iron (plus holes) in the drop; Figure 28 shows a sulfur map, with no sulfur penetrating to the steel.

The SEM photomicrographs of the interface between an Illinois #6 LTA drop adhered to oxidized stainless steel in air are illustrated in Figure 29. The appearance is similar to the adhesion on the oxidized T-11, except that a substrate temperature of 600° C was necessary to develop a thin oxide film and to produce a significant adhesion strength.

Previous experience has shown that pyrite and 75% pyrite-25% clay mixtures gave strong adherence under oxidizing conditions.¹⁹ Figure 30 is the SEM photomicrographs showing the interface of a drop of 75% pyrite - 25% kaolinite mixture on oxidized T-11 steel at 500° C. The drop wetted the oxide layer on the steel, giving a smooth interface between the drop and steel. A fracture was produced between the oxide layer and the steel upon cooling to room temperature. The drop also cracked at the interface. The SEM-EDS analysis revealed that the drop was very heterogeneous, since a layer containing only iron and sulfur existed at the bottom of the drop.

Figure 25. X-ray profiles of various elements as a function of distance from the interface, oxidized T-11 steel substrate at left and Illinois #6 LTA drop at right.

(a)

Figure 26. Backscattered electron image of interface between Illinois #6 drop (at right) and oxidized T-11 steel substrate (at left).

(b)

Figure 27. Iron x-ray mapping of interface shown in Figure 26.

(c)

Back scattered electron (a) and the corresponding iron x-ray mapping (b) and sulfur mapping (c), showing cross-section characteristic of the interface between Illinois #6 drop (at right) and oxidized T-11 steel substrate (at left).

Figure 28. Sulfur x-ray mapping of interface shown in Figure 26.

Figure 29. SEM photomicrographs showing cross-section characteristic of interface between Illinois #6 LTA drop and oxidized 304 SS stainless steel substrate. Magnification of (b) fifteen times that of (a).

Figure 30. SEM photomicrographs showing cross-section characteristic of interface between 75% pyrite plus 25% kaolinite drop and oxidized T-11 steel substrate. Magnification of (b) twenty times that of (a).

The sticking behavior under reducing conditions was used to evaluate the nature of the adhesion of slag drops on the reduced T-11 surface. Drops from Illinois #6 and Upper Hiawatha #1 LTA did not adhere to the reduced surface, but drops from these materials gave strong adherence at 500° C on oxidized steel surfaces. Drops formed from the pyrite - kaolinite mixture gave an adhesion force of 95 g at 500° C on the reduced surface, compared with an adhesion force of 1000 g on the oxidized steel surface at the same temperature.

A comparison of SEM photomicrographs of the oxidized and reduced surfaces is given in Figure 31. Both surfaces are microporous, but the reduced surface appears to have a higher porosity with larger pores. Figure 32 shows SEM photomicrographs of the polished sections on the oxidized steel and on the reduced steel. The structure of the drop shows a surface layer at the interface which contains only Fe and S (by SEM-EDS); glass containing Al, Si, and Fe in the center; plus some regions of mechanical mixture of base components. Apparently the low melting point of FeS enables a drop to be formed and fall without sufficient time for uniform reaction of the base components. Thus the actual material at the interface is FeS. The FeS is compatible with the oxide layer and wets the layer, but there is no evidence for penetration into the pores to give mechanical anchoring. The contact between the drop and the reduced surface is much less compatible and there is again no evidence for mechanical anchoring in the microporosity.

(a)

(b)

Figure 31. SEM photomicrographs of (a) the oxidized steel surface; and (b) the reduced steel surface.

Figure 32. SEM photomicrographs of the polished cross-section of ash drop on (a) oxidized steel surface and (b) reduced steel surface.

Figure 33 gives clear evidence of hemispherical particles spread on the oxide layer, forming the initiating layer. This photomicrograph is of a deposit produced from the Powder River Basin coal from Suite 1. The flattened particles were analyzed by SEM-EDS. The spectra showed significant amounts of Na, Mg, Al, Si, S, Ca, Ti, and Fe, with major peaks for Ca and Fe. Analysis of the locations higher in the deposit gave major peaks for Ca, Al, Si, and Fe, but neither Na nor S were seen in the higher regions.

Application of the same techniques to the strongly adherent material of the high-rank coals showed that there were essentially four classes of particles with characteristic chemical compositions involved in the strongly adherent materials:

Type 1. Highly porous black particles with a rough surface texture were prominent. This type of particle contained mostly Fe with traces of Al and Si.

Type 2. Glassy black spheres with smooth surface texture were also found. This type of particle contained Fe and smaller concentrations of Al, Si, K, Ca, and Ti with a trace of S.

Type 3. Glassy transparent spheres with a smooth surface texture. This type of particle gave large EDS peaks for Ca and Fe, with smaller peaks for Al and Si.

Type 4. Black particles with a smooth surface texture

Figure 33. Strongly adherent particles forming an initiating deposit layer: deposit from Powder River Basin coal.

containing Al and Si with a trace of Fe.

Types 1 and 2 made up most of the adherent layer from the high-rank coals, with a few Type 3. Type 4 was found only in the adherent layer from the deposit produced from Pittsburgh #8, along with the other types. The black particles of Type 1 were often deformed and flattened against the oxide film of the substrate, showing that the particles were molten on impact.

For the low-rank coals, Type 3 particles were predominant in the adherent material of the deposit. These high Ca and Fe content particles showed much less deformation, retaining more of the spherical shape even in contact with the oxide layer, indicating that these particles were sticky but had high viscosity upon deposition. These particles usually did not show significant concentrations of Na or S.

A synthetic coal containing only illite formed a large deposit, probably due to the importance of a low melting point glass phase forming sticky particles, thus allowing for accumulation and growth of a massive deposit. (The sticking process is discussed in detail in the next section.) However, little material adhered after the deposit was brushed off the oxidized steel substrate, indicating that the glassy material from illite did not strongly adhere to the iron oxide layer on the substrate. Previous results from the sticking test using illite confirm this observation; the sticking temperature of the

illite drop was relatively high (450°C) and the adhesion force at 500° was very weak (about 2 grams).¹⁹ In contrast, the deposit from synthetic coals containing only pyrite or a mixture of pyrite and clay gave a significant amount of adherent material. This observation is also in agreement with previous results of the sticking test which showed a low sticking temperature of 250° and a high adhesion force at 500° of 100 grams.¹⁹ The adherent material was found to be rich in iron, suggesting that pyrite in coals leads to the formation of a strong initial deposit layer as well as a strong deposit mass.

The synthetic coals containing mixtures of pyrite and clays (illite and kaolinite) gave larger and stronger deposits than the deposit from the synthetic coal containing only pyrite. A high iron content but only a trace of glassy phase, probably formed from clays, were detected by x-ray diffraction analysis of these deposits. This observation suggests that most of the pyrite but not clays leads to formation of a deposit under these conditions. However, since the iron-rich fly ash contains a small amount of glass, this composition was therefore more likely to adhere and sinter, resulting in a significant deposit build-up.

The adhesive strength of small particles (i.e., about 100 micrometers in diameter) was measured by an attachment for the deposit strength apparatus. The design and construction of the strength apparatus is given in detail in the section on development of deposit strength. For measuring adhesive strengths

of small particles the apparatus is attached to the stage of an optical microscope. A needle of small blade is attached to the end of the rod, which is then used as a ram to shear off the particle at room temperature. The pressure exerted to shear the particle is measured; results are reported based on the total area of contact to the oxide layer. This apparatus was used to study adherent particles produced in combustion of the Suite 2 coals. SEM-EDS analyses of the adherent particles were performed prior to measurements of the adhesive strengths of the same particles.

Adherent particles from Center lignite mostly contained significant quantities of calcium and sulfur, probably as calcium sulfate. These particles have adhesive strengths of 3.0 - 3.7 MPa. The particle having the highest adhesive strength contains high concentrations of iron and silicon, possibly as fayalite (Fe_2SiO_4) which has a low melting point of 1200°C . The quantity of adherent particles was greatly reduced when testing Center lignite from which the cations had been removed by ion exchange. The ion-exchange procedure removed calcium present as carboxylate salts or as soluble sulfates (i.e., gypsum). The substrate from the test with ion-exchanged lignite produced proportionately more adherent particles rich in iron but fewer total adherent particles.

Most of the adherent particles in deposits from San Miguel lignite which showed high adhesive strengths contained high

concentrations of iron and silicon. Similar particles were present in deposits produced from Martin Lake lignite.

The comparison of adherent particles produced from Rosebud subbituminous coal with those from the 1.4 specific gravity float and 1.6 s.g. sink fractions of the same coal enabled the isolation of adherent particles specific to each gravity fraction. The 1.4 s.g. float fraction produced a very small quantity of adherent particles. The particles are about 18 to 25 micrometers in diameter. Some have high concentrations of calcium and phosphorus, possibly as a calcium phosphate. (However, no significant enrichment of phosphorus is noted in the ash analysis of the 1.4 s.g. float.) Magnesium is also abundant in the adherent particles from the 1.4 s.g. float. Unfortunately the particles were too small to obtain adhesive strength measurements. A test with the 1.6 s.g. sink fraction produced numerous large adherent particles, many of which contain significant quantities of sulfur and iron. The presence of sulfur is due to insufficient residence time in the hot zone to facilitate complete decomposition and oxidation of pyrite in the coal to iron oxides. The adhesive strengths of the iron sulfide particles range from 2.2 - 4.6 MPa. A particle containing mostly iron and silicon had the highest adhesive strength, 7.1 MPa.

For all the coals examined, the ash particles that have the highest adhesive strengths appear to be those rich in iron and silicon. Strengths ranged from 7.1 - 76 MPa. The next group of

particles that exhibit a measurable strength of adhesion contain iron and sulfur and have adhesive strengths ranging from 2.2-4.6 MPa. The final group of particles that have measurable strength of adhesion are those rich in calcium and sulfur, having strengths of 3.0 - 3.7 MPa. Other types of adherent particles were also identified but no data on adhesive strengths was obtained; these particles include ones rich in barium and sulfur; in barium, strontium, and sulfur; in calcium and phosphorus; and in iron.

To place these strength measurements into some context, the strength of adhesion of epoxy resin on steel can be as high as 40 MPa and that of enamel coatings on metals can exceed 50 MPa.²¹ It has been estimated that an adhesive bond of 0.1 kPa is able to support the weight of a 10 mm thick lightly sintered ash deposit having a density of 1000 kg/m³.¹⁴

Build-up of the Deposit: The Sticking Process

Table 42 gives the deposit rates for the Suite 1 coals when 10 g of each coal was fed to the furnace over a period of 30 minutes. Figure 34 shows the variation of deposit mass with time. As the deposit grows, the rate of deposition increases, since the top of the growing deposit will become increasingly hotter. Figures 35 and 36 show the deposition rates estimated by differentiation of the curves in Figure 34, normalized by dividing the rate of firing of high temperature ASTM ash in the

Table 42. Deposit mass and percent ash recovered as deposit for test coals: total coal feed = 10 g; feed time = 30 min.

Coal	ASTM ash, [*] wt. %	Height of deposit, cm	Deposit mass, mg	Ash recovered as deposit, %
<u>Normal constrictor (1.27 cm dia.)^a</u>				
Illinois #6	17.4	1.5	1066	62
Pittsburgh #8	8.7	0.7	600	69
U. Hiawatha #1	9.4	1.4	568	60
U. Freeport	17.1	3.0	1254	73
Tunnelton	15.8	0.9	446	28
Decker	4.0	1.0	132	33
Powder River Basin	4.6	1.0	320	65
Texas	18.9	2.0	1197	63
N. Dakota	7.1	1.3	367	52
<u>Normal constrictor (3.18 cm dia.)^b</u>				
U. Hiawatha #1	9.4	0.3	424	45
<u>60° angled constrictor (1.27 cm dia.)^a</u>				
U. Hiawatha #1	9.4	1.9	380	40
Powder River Basin	4.6	2.0	223	49
N. Dakota	7.1	2.0	202	29

* high temperature ash determined from 60x325 mesh coal

^a Gas velocity through constrictor = 3.5 m/sec.

^b Gas velocity through constrictor = 0.6 m/sec.

Figure 34. Weight of deposit versus time: coal feed rate = $1/3$ g/min.; excess air = 20 %; furnace temperature = 1500°C ; substrate temperature = 500°C ; gas temperature at the location 2 cm above the substrate = 1300°C ; gas velocity through the normal constrictor = 3 m/sec.

Figure 35. Deposit rate as a fraction of ash (ASTM) firing rate, versus deposition time: high-rank coals; coal feed rate = 1/3 g/minute; excess air = 20%; furnace wall temperature = 1500 °C; substrate temperature = 500 °C; gas temperature at the location 2 cm above the substrate = 1300 °C; gas velocity through the constrictor = 3 m/sec.

Figure 36. Deposit rate as a fraction of ash (ASTM) firing rate, versus deposition time: low-rank coals; coal feed rate = 1/3 g/minute; excess air = 20%; furnace wall temperature = 1500 °C; substrate temperature = 500 °C; gas temperature at the location 2 cm above the substrate = 1300 °C; gas velocity through the constrictor = 3 m/sec.

0.33 g/min of coal. These Figures emphasize the differences in the way the deposit grows. For example, Illinois #6 shows a strongly accelerated rate of growth, whereas Tunnelton and the low-rank coals show a more uniform rate of deposition. Most of the bituminous coals, except Tunnelton, reached a sticking coefficient close to 1 at the end of the deposition time of 30 minutes, showing that when the deposit reaches a certain height, the top of the deposit can give virtually complete capture of the fly ash. (The sticking coefficient, also called the sticking fraction, is defined as the actual deposit weight divided by the quantity of ash fed based on the ASTM ash determination.) However, at longer deposition times (up to 90 minutes), the sticking coefficient decreases, probably because the changing of the deposit shape as the deposit grows alters the flow of gas around the deposit. Consequently, there appears to be a fraction of fly ash entering the nozzle that simply by-passes the deposit. The behavior of Upper Freeport and Tunnelton is remarkable in that the coals have almost identical ash compositions, yet give entirely different deposition behavior.

The gas - particle stream was accelerated as it passed through the constrictor. The deposit formed on the substrate at the point where the gas - particle stream underwent a sharp change in direction. Most of the molten or sticky particles could stick nearer to the center of the substrate, whereas less sticky particles move on with the gas stream. The deposit forming at the center of the substrate had, therefore, the typical appearance of

a cone that grows in the direction of the incoming hot gases, as illustrated in Figure 37. It was quite easy to see the direction of gas flow indexed by the growth lines in the deposit. This provides evidence that the mechanism of growth is direct head-on impingement, while particles skimming a surface may not stick to it.

For the coals in Suite 2, the North Dakota lignites showed a gradually increasing to even growth rate, as shown in Figures 38 and 39. The Indian Head and Beulah lignites showed a more even rate of growth compared to the Center and Velva lignites. This difference may be due to the higher concentrations of sodium in the Indian Head and Beulah lignites, the sodium being likely to form very small particles which would follow the gas streamlines and not be deposited.

The Gascoyne lignite samples were from different pits within the same mine. The plots of deposit weights as a function of time are given in Figures 40 and 41. The White and Yellow pit samples have higher sticking fractions than the Blue and Red samples. The White pit sample showed an accelerated growth rate. The morphology of the deposit produced from this sample was indicative of abundant liquid having been present at the top of the deposit; the liquid would create a captive surface which would retain most particles striking it.

The subbituminous coals in Suite 2 generally showed a

Figure 37. Appearance of deposit for (a) Upper Freeport; (b) Illinois #6; (c) Pittsburgh #8; (d) Upper Hiawatha #1; and (e) Tunnelton.

(a)

(b)

(c)

(d)

Figure 37. Appearance of deposit for (a) Texas; (b) Decker; (c) North Dakota; and (d) Powder River Basin.

Figure 38. Deposit weight versus time for selected North Dakota lignites from different mines: coal feed rate 0.2-0.4 g/min; 20% excess air; hot zone temperature = 1500°C; gas temperature at constrictor ~1260°C; gas velocity across substrate 3-4 m/sec.
(○- Beulah; ●- Velva, □- Indian Head, and ▽- Center.)

Figure 39. Sticking coefficient versus time for selected North Dakota lignites from different mines: coal feed rate 0.2-0.4 g/min; 20% excess air; hot zone temperature = 1500°C; gas temperature at constrictor ~1260°C; gas velocity across substrate 3-4 m/sec. (1 - Beulah, 2 - Velva, 3 - Indian Head and 4 - Center)

Figure 40. Deposit weight versus time for Gascoyne North Dakota lignites from different pits: coal feed rate 0.2-0.4 g/min; 20% excess air; hot zone temperature = 1500°C; gas temperature at constrictor ~1260°C; gas velocity across the substrate 3-4m/sec. (▽ - Gascoyne Red, Δ - Gascoyne White, □ - Gascoyne Blue and ○ - Gascoyne Yellow.)

Figure 41. Sticking coefficient versus time for Gascoyne North Dakota lignites from different pits: coal feed rate 0.2-0.4 g/min; 20% excess air; hot zone temperature = 1500°C; gas temperature at constrictor ~1260°C; gas velocity across substrate 3-4 m/sec. (1- Gascoyne Red, 2 - Gascoyne White, 3 - Gascoyne Blue, and 4 - Gascoyne Yellow.)

behavior similar to that of the North Dakota lignites.. However, the sticking fraction shows a gradual increase at the initial stages of deposit formation and then appears to drop slightly (Figure 42). Two factors may account for this behavior of the sticking fraction; First, changes in the flow patterns of the gas stream, caused by deposit growth, may decrease the possibility of fly ash impaction. Second, these deposits did not appear to have been fused at the top, so there may have been no significant quantity of molten material present to produce a captive surface.

The sticking fraction as a function of time is plotted for Martin Lake and San Miguel lignites in Figure 43. The much higher sticking fraction of the San Miguel may reflect differences in the mode of occurrence of the inorganic constituents in the two lignites. Zeolites have been identified as principal mineral components of San Miguel lignites.²² These zeolites can contain significant quantities of sodium, which can reduce the melting point and enhance the formation of very sticky, partially molten particles, resulting in the observed high sticking fraction. In comparison, Martin Lake lignite has a similar range of inorganic constituents to some North Dakota lignites, in which the alkali and alkaline earth elements are associated with the organic portion of the coal.

The removal of ion-exchangeable cations from Center lignite resulted in only a small decrease in deposit weight and no significant difference in the sticking fraction. However, with

Figure 42. Sticking coefficient versus time for subbituminous coals: coal feed rate 0.2-0.4 g/min; 20% excess air; hot zone temperature = 1500°C; gas temperature at the constrictor ~1260°C; gas velocity across the substrate 3-4 m/sec.
(1- Rosebud, 2 - Dave Johnston, 3 - Wyodak and 4- Navajo.)

Figure 43. Sticking coefficient versus time for Texas lignites: coal feed rate 0.2-0.4 g/min; 15-25% excess air; hot zone temperature = 1500°C; gas temperature at constrictor ~1260°C; gas velocity across substrate 3-4 m/sec.
(1 - Martin Lake and 2 - San Miguel.)

San Miguel lignite a marked change in sticking fraction was observed in tests with the ion-exchanged sample (Figure 44). The difference in behavior of the ion-exchanged San Miguel and Center lignites may again reflect differences in the association of the inorganic constituents. During combustion in the short residence times of the drop-tube furnace, low melting point species are more likely to form if the alkali is already in direct contact with the aluminosilicate minerals. This is the case with the zeolite minerals in San Miguel lignite. On the other hand, interaction of alkali with aluminosilicates may be less likely in the case of Center lignite because of volatilization of some of the organically bound alkali.

For Rosebud subbituminous coal and its various float/sink fractions, the 1.6 s.g. sink fraction had the highest sticking fraction. This fraction contains considerable quantities of iron, which result in the formation of sticky, high density particles. The sticking fraction for the 1.4 s.g. float was almost as high; this fraction contains the highest quantities of alkali and alkaline earth elements, which are likely to react with silicates to form very sticky particles.

Development of Deposit Strength by Sintering

An apparatus was developed to measure strength of deposits. The apparatus is shown in Figure 45. The primary components are a miniature pressure transducer and a miniature horizontal

Figure 44. Sticking coefficient versus time for San Miguel and ion-exchanged San Miguel: coal feed rate 0.2-0.4 g/min; 20% excess air; hot zone temperatures = 1400 and 1500°C; gas temperature at the constrictor ~1260°C; gas velocity across the substrate 3-4 m/sec.
(1 - San Miguel 1400°C, 2 - San Miguel 1500°C, 3 - ion-exchanged San Miguel 1400°C, 4 - ion-exchanged San Miguel 1500°C.)

Figure 45. Translator/transducer assembly with deposit strength measuring device.

translator. The translator has a range of travel of 25 mm, a resolution of 0.02 micrometer, and a maximum speed of 15 mm/min. The pressure transducer is a diaphragm strain gauge with one active sensing face. The output of the transducer is attached to a strain indicator. The transducer was mounted in a machined aluminum block attached to the horizontal translator. A hole drilled in the block allows the end of a 3 mm steel rod to make contact with the sensing face of the transducer. The strength of deposits can be determined by compressing the deposit between the end of the steel rod and the aluminum block attached to the base plate. The translator is set in motion and the pressure exerted to crush the deposit is measured. Measurements can be made at 3-6 mm intervals across the deposit.

Deposit strengths were measured for deposits produced from all Suite 2 coals tested except for Navajo, for which the deposit strength was below the detectable limits of the device. The maximum limit of the pressure transducer was 7 MPa; some deposit strengths exceeded this upper limit. Strengths were measured at selected intervals (3 - 6 mm) from the base to the top of the deposit. Strengths for some North Dakota lignite ash deposits are shown in Figures 46 and 47. Deposit strengths for the subbituminous coals are plotted as a function of height in Figure 48.

The Wyodak and Dave Johnston coals have very similar ash compositions, yet produce deposits of quite different strengths.

Figure 46. Deposit strength versus deposit height for North Dakota lignite deposits produced at a hot zone temperature of 1500°C and a constrictor gas temperature of approximately 1260°C.
 (○ - Beulah, ● - Velva, □ - Indian Head, and ▽ - Center.)

Figure 47. Deposit strength versus deposit height for Gascoyne North Dakota lignite deposits produced at a hot zone temperature of 1500°C and gas temperature at the constrictor of approximately 1260°C.
(□ - Gascoyne Blue, Δ - Gascoyne White, ∇ - Gascoyne Red, and ○ - Gascoyne Yellow.)

Figure 48. Deposit strength versus deposit height for subbituminous coal deposits produced at a hot zone temperature of 1500°C and a constrictor gas temperature of approximately 1260°C.
(○ - Dave Johnston, ● - Wyodak, and
△ - Rosebud.)

The Wyodak ash contains less silica than the Dave Johnston ash. This observation suggests that the principal silicon-containing minerals present in Wyodak are clays, or at least different types of clays than are found in the Dave Johnston coal. The significance of this difference is that clay minerals appear to become completely melted during combustion whereas quartz may not melt or react completely. The quartz content of a coal can be estimated from the equation

$$(\text{SiO}_2)_q = (\text{SiO}_2)_t - 1.5(\text{Al}_2\text{O}_3)$$

The subscripts q and t represent quartz and total silica, respectively. This equation is based on data for British bituminous coals which indicates that the clay minerals have an average alumina/silica weight ratio of 1.5.²³ Thus the term $1.5(\text{Al}_2\text{O}_3)$ corrects the total silica content for the amount of silica incorporated in clays; the difference being the silica present as quartz. Applying this equation to the Wyodak and Dave Johnston coals shows quartz contents of 2.0% and 15.1%, respectively. Compared to the Dave Johnston coal, the clay minerals in Wyodak will react much more readily with the available alkali and alkaline earth elements and may form more liquid phase, resulting in increased viscous flow sintering and thus producing a stronger deposit.

Strength measurements for Rosebud and its float/sink fractions are shown in Figure 49. The 1.4 s.g. float fraction produced the strongest deposit. The alkali and alkaline earth elements and finely divided clay minerals concentrate in the

Figure 49. Deposit strength versus deposit height for Rosebud subbituminous coal and float-sink fractions produced with a hot zone temperature of 1500°C and a constrictor temperature of approximately 1260°C. (○ - 1.6 Sink, ● - 1.4 Float, □ - 1.6 Float, and △ - Starting coal.)

float fraction. The relatively high strength in this deposit is due to the formation of low melting point phases as a result of this association of elements and clay minerals. On the other hand, minerals such as quartz, pyrite, and large agglomerates of clay minerals concentrate in the 1.6 s.g. sink fraction. The sink fraction produces the weakest deposit because of the low concentration of alkali and alkaline earth elements available for reaction with the minerals.

The effect of removing cations from Center and San Miguel lignites by ion-exchange was to produce deposits weaker than those from the untreated coals. Furthermore, deposits produced in combustion tests with hot zone temperatures of 1500°C were stronger than deposits from tests with hot zone temperatures of 1400°, regardless of whether the coal had been ion-exchanged.

It has long been established that for Western coals the tendency for ash deposition is strongly related to the sodium content of the coal.²⁴ The strength of deposits, expressed as MPa/mm, is plotted as a function of sodium content, expressed as Na₂O in the ash, in Figure 50. Although there is appreciable scatter in the data, it appears that there is a maximum or levelling off at approximately 8.8% Na₂O. It is interesting to note that a plot of ash deposition (e.g. as weight of deposit collected on simulated heat exchange tubes in a pilot scale combustor) as a function of sodium also levels off in the region of 8 - 8.5% Na₂O²⁴. This comparison suggests a relationship,

Figure 50. Deposit strength/deposit height ratio versus sodium content of the ASTM ash (hot zone temperature = 1500°C, constrictor gas temperature ~1264°C).

albeit still tenuous, between the growth of strength in a deposit and the ability of a large deposit mass to form on tubes.

SEM-EDS analyses were used to examine the microstructure of polished cross-sections of deposits and to determine the morphological and compositional changes that occur from the base of the deposit to the top. Backscatter electron imaging was used to distinguish between crystalline and glassy phases present. Analyses of points and areas were performed to determine the composition of the glassy and crystalline phases. A compilation of the microphotographs and extensive tables of the analytical results have been published elsewhere.²⁵ The principal conclusions of this work will be presented here.

The formation of crystalline material appears to be an indication of the degree of interaction between ash-forming species within the ash deposits. Some of the strongest deposits examined contained abundant crystals such as pyroxene and melilite. In these strong deposits the sodium concentrates in the glass phase; thus sodium would be expected to reduce the viscosity of the liquid phase, resulting in increased deposit strength.

Deposit strength development is primarily due to viscous flow sintering. The rate of sintering can be determined by the following equation²⁶

$$S_r = k_1(R_g/c)(1/V)$$

where R_g/c is the ratio of glass to crystalline material and V is the viscosity of the glass. The glass is primarily responsible for viscous flow sintering and thus is responsible for development of deposit strength.

The viscosity of the glass phase was calculated from the composition of the glass determined by SEM-EDS analysis; calculations were done using the modified Urbain equation developed for low-rank coal ash slags.²⁷ Composition data and calculated viscosities are summarized in Table 43. The maximum strength observed in a deposit is plotted as a function of calculated liquid viscosity in Figure 51. The deposit strength shows an inverse relationship to the viscosity of the glass phase, which is consistent with viscous flow sintering theory.

The partitioning of sodium during combustion to form solid, liquid, and gas phase species is very important with regard to boiler slagging and fouling, especially for the Western coals. The interaction of sodium with sulfur and silicates produces low melting point phases and thereby increases both the stickiness of ash particles and the quantity of low-viscosity liquid available for sintering. Equilibrium calculations were used to predict the variation of sodium-containing species in the gas and liquid phases as a function of temperature. The calculations were performed using the computer program SOLGASMIX, which calculates complex phase equilibria by free energy minimization.^{28,29,30} The program has been adapted for use on an IBM-PC computer.³¹

Table 43. Composition and viscosity of glass phase determined by SEM-EELS analysis for lignites.

<u>Oxide</u>	<u>Beulah</u>	<u>Gascoyne Red</u>	<u>Gascoyne White</u>	<u>Gascoyne Blue</u>	<u>Gascoyne Yellow</u>	<u>Center</u>	<u>Velva</u>
SiO ₂	47.2	55.1	59.7	55.7	50.4	43.9	46.9
Al ₂ O ₃	16.8	9.3	10.2	10.4	14.7	17.9	15.9
Fe ₂ O ₃	6.8	6.0	0.9	3.7	2.1	3.8	5.1
TiO ₂	0.7	1.9	3.1	0.7	1.3	0.3	0.7
P ₂ O ₅	1.2	0.2	0.0	0.0	0.0	0.0	0.0
CaO	16.6	20.3	16.4	17.4	20.9	20.8	25.6
MgO	0.2	3.9	2.5	3.3	9.4	5.8	3.9
Na ₂ O	7.2	1.1	5.3	7.5	0.4	4.2	0.7
K ₂ O	0.2	0.2	0.5	0.2	0.2	0.9	0.4
SO ₃	0.2	0.3	0.2	0.2	0.2	1.0	0.2
Viscosity at 1300°C (PaS)	80	154	123	203	93	48	60

Table 43. Composition and viscosity of glass phase determined by SEM-EDS analysis for subbituminous coals.

<u>Oxide</u>	<u>Rosebud</u>	<u>Wyodak</u>	<u>Dave Johnston</u>
SiO ₂	77.2	50.8	51.6
Al ₂ O ₃	15.4	27.5	31.9
Fe ₂ O ₃	2.4	1.4	1.6
TiO ₂	0.5	0.0	0.2
P ₂ O ₅	0.0	0.0	0.0
CaO	2.0	18.6	12.5
MgO	0.6	0.4	0.7
Na ₂ O	0.3	0.6	0.2
K ₂ O	1.3	0.2	1.1
SO ₃	0.0	0.2	0.0
Viscosity at 1300°C (PaS)	677	321	500

Figure 51. Deposit strength versus viscosity of the glass phase for 10 selected lignite and subbituminous coals.

In a simple case, using only thermodynamic data for compounds of the elements Na, Si, S, O, N, H and C, the major sodium-containing gaseous species were predicted for Gascoyne White lignite. The results are shown in Figure 52. These results agree well with predictions made by other investigators.³² The distributions of sodium-containing liquids are shown in Figure 53. The most abundant sodium-containing liquid up to 1340 K (1067°C) is Na_2SO_4 ; at higher temperatures $\text{Na}_2\text{Si}_2\text{O}_5$ is the most abundant.

By expanding the thermodynamic data base to include the elements Na, Mg, Al, Si, S, Ca, Fe, O, N, and H, and their compounds the predictions change somewhat. For the gaseous species the only change is a reduction in the amount of Na_2SO_4 predicted. However, for the liquid phase $\text{Na}_2\text{Si}_2\text{O}_5$ is no longer predicted to be the most abundant sodium-containing liquid; rather, the most abundant species are predicted to be NaAlSiO_4 and $\text{NaAlSi}_3\text{O}_8$. The predicted formation of the aluminosilicates rather than silicates suggests that the aluminosilicates form preferentially to the reaction of sodium with silica above 1100 K. At lower temperatures Na_2SO_4 becomes the dominant sodium-containing liquid phase.

Obviously the relative abundance of the various species predicted by SOLGASMIX will be influenced by the composition of the coal. For example, with Center lignite, which contains higher

Figure 92. Sodium-containing gaseous species predicted to form during the combustion of Gascoyne White lignite at 20% excess air using equilibrium data set Na-Si-S-O-N-C.

Figure 53. Distribution of sodium-containing liquid species predicted to form during the combustion of Gascoyne White lignite at 20% excess air. Predicted using equilibrium data set Na-Si-S-O-N-C.

concentrations of the alkali and alkaline earth elements and lower amounts of silicon than the Gascoyne White, high concentrations of Na_2SO_4 were predicted up to nearly 1700 K (1427° C). Such silicates and aluminosilicates as $\text{NaAlSi}_3\text{O}_8$, $\text{NaAlSi}_2\text{O}_6$, and $\text{Na}_2\text{Si}_2\text{O}_7$ are present in mole fractions less than 10^{-5} .

The influence of sodium on the stability of the major species formed during combustion of Gascoyne Yellow lignite was modeled by running a series of SOLGASMIX calculations in which the input value of the Na_2O content of the ash was increased by 1.5 wt.% for each successive calculation. The major liquid species predicted to form at 1600 K are plotted as a function of sodium content in Figure 54. As the concentration of sodium is increased the predicted amount of sodium-containing silicates first increases, then passes through a broad maximum and eventually declines. With respect to the solid phases, the mole fraction of gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$, increases with increasing sodium content, while akermanite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$, remains essentially constant. Unfortunately, thermodynamic data for sodamelilite could not be found; the inclusion of this species in the calculations could have an influence on the predicted abundances and relative stabilities of the other solid and liquid phases.

The quantity and composition of the liquid phase produced during combustion of the Suite 2 coals was predicted for those coals for which SEM-EDS characterization had been performed on

Figure 54. Influence of sodium content on the distribution of liquid species predicted to form upon combustion of Gascoyne Yellow coal using equilibrium data set Na-Mg-Al-Si-S-Ca-Fe-O-N.

the deposit cross-sections. The composition of the liquid phase was determined by normalizing the sum of the mole fractions of each of the major constituents to 100%. Reasonably good preliminary predictions of the composition of the liquid phase, as compared to actual SEM-EDS analysis, could be made for coals with ashes having base-to-acid ratios less than 1.2. Problems with the calculations were encountered for coals of greater than 1.2 base-to-acid ratio in the ash and for coals having high concentrations of calcium. The deposit strength is plotted as a function of the predicted quantity of liquid in Figure 55. Deposit strength increases with increasing quantity of liquid phase.

Figure 55. Deposit strength versus predicted quantity of liquid in deposits (1300°C).

CONCLUSION

Ash particles and the gaseous products of combustion are accelerated to about 3 - 4 m/sec and impinged on a water-cooled oxidized boiler steel substrate held at 500°C. The gas stream undergoes a sharp change in direction upon encountering the substrate. This change creates a higher gas velocity in the direction of the incoming hot gases toward the center of the substrate compared to that flowing around the substrate. A deposit begins to form due to the impingement of particles and flue gas on the substrate. The principal mechanism of particle transport to the surface of the substrate is by inertial impaction, as indicated by the average size of ash particles in the deposit being much larger than the particles in the dust around the deposit mass. Many particles may impact and rebound, but some will stick to the surface of the steel and form a strong bond with the oxide layer. These strongly bonded particles are thought to be characteristic of those that cannot be removed by conventional soot-blowing techniques from full-scale utility boiler water walls. The ability of these particles to stick to the boiler steel surface depends upon the melting behavior, surface tension, and wetting ability of the ash particle, and the nature of the boiler steel surface. The particles that form the strongest bonds are rich in iron and silicon, followed by those rich in iron and sulfur.

A very thin (less than 1 mm) dust layer forms over the entire surface of the substrate. This layer consists of very small particles possibly transported across the boundary layer due to vapor-phase and small-particle diffusion, thermophoresis, and electrophoretic effects. These particles could be easily removed and were not bonded to the surface. The dust layer is primarily composed of sodium, magnesium, calcium and sulfur. This layer probably continues to form throughout the duration of the test.

The initiation of deposition is by the adherence of molten ash droplets to the oxide layer of the substrate. Upon impinging on the cool substrate, ash droplets solidify rapidly and only a fraction of the droplets adhere with sufficient strength to the oxide layer. Several small islands of adhered particles may form; this creates more roughness to the surface for further deposition. In shear tests it was frequently found that rather than the particle breaking off the oxide layer, the oxide layer was broken off the substrate. This observation indicates that adherence between the oxide layer and the initial layer of the deposit was stronger than the adherence of oxide layer to the metal. The very weak adhesion of ash drops on a porous reduced steel surface indicates that strong adhesion of ash drops occurs as a result of chemical compatibility between the oxide layer and the ash drop, and is not a result of mechanical anchoring in the microporosity of the steel surface. The strong adherence between the initial layer of ash drops and the oxide layer is probably

due to a good wetting and a large contact area of the hemispherical droplets on the oxide layer, allowing chemical compatibility at the interface. It also seems likely that the oxide layer on the substrate reduced the rate of heat conduction away from the interface and kept the ash drop less viscous for a longer time, again allowing more chemical compatibility at the interface.

As the deposit grows the temperatures of the deposited material increase, thus increasing the ability of trapping oncoming fly ash particles. The deposit begins to grow from the substrate at the point where the gas stream impinges on the base layer. The dust layer easily separates from the base layer of the deposit. The base layer is lightly sintered due to the higher temperatures encountered when moving away from the substrate. The degree of crystallinity of the base layer is similar to that of the fly ash, which indicates that very little interaction between particles has occurred. To some extent this lower portion of the deposit is insulated by the upper layers of the growing deposit and thus remains only slightly sintered due to the relatively low temperatures in this region. The mechanical strength of the base is lower than that of the upper regions of the deposit. The quantity of base layer formed is dependent on the type of coal being fired. A qualitative relationship suggests that coals which contained large quantities of organically bound alkali and alkaline earth elements and few clay minerals or quartz produced the largest quantity of base layer in the deposit.

As particles continue to impact the base, the deposit mass grows in the direction of the oncoming gas stream. The higher temperatures produce more melted and fused material which can act as a captive surface to collect particles that impact the surface. The formation of a captive surface drastically increases the growth rates. When the deposit reaches a certain height, the top of the deposit may give virtually complete capture of the fly ash (i.e., sticking fraction = 1). However, as the deposit grows toward the constrictor, the changing of deposit shape alters the flow of gas around the deposit. Consequently, there may be a fraction of the fly ash entering the constrictor that simply passes over the deposit. The rate of deposit growth can be expressed in terms of variation of sticking fraction with time. Most of the bituminous coals tested exhibited an accelerated rate of growth, whereas most of the low-rank coals showed a more uniform rate of deposition. Low-rank coal deposits in which abundant molten material existed exhibited an accelerated rate of growth.

The variation of sticking fraction with time is distinctive for each coal. It is hypothesized that different coals have different sticking coefficients for the following reasons:

- a) The proportion of fly ash particles which are molten or solid but sticky is different for different coals;
- b) The size distribution and density of fly ash particles produced from different coals are different;

c) The physical and chemical characteristics of the deposit mass formed from different coals are different due to differences in the sintering, chemical reaction, and melting behaviors of the particles after deposition.

The temperature gradient in the deposit mass causes the processes of sintering, chemical reaction and melting to occur at different rates at different locations in the deposit. The extent of these processes increases toward the hot top of the deposit. Hence the deposit has a microstructure leading from the slight sintering of the lower layers to the strongly melted top. The lower layers of deposits from bituminous and low-rank coals showed a close similarity in the size, shape, and chemical composition to that of the fly ash. However, a higher amount of glassy phase was observed at the top of the deposits from bituminous coals, whereas a higher amount of crystalline phase occurred at the top of the deposits from low-rank coals.

As the deposit grows and is exposed to higher temperatures (i.e., $>1000^{\circ}\text{C}$) low-viscosity liquids are formed in the deposit. These low-viscosity liquids are responsible for the development of deposit strength due to sintering. The deposits that appeared to contain the most fused and sintered material were the strongest. The strongest deposits produced from Western coals contained massive fused regions near the top, with abundant crystal growth. The weak deposits characteristically have high porosity, indicating that the degree of sintering and fusing of

the ash particles was not as extensive.

As the sintering process continues, crystallization of complex aluminosilicates from the melt phase begins. The crystals mainly consist of alkali and alkaline earth aluminosilicates, such as pyroxenes, melilites, and plagioclase. These phases form as a result of the melting and interaction of quartz and clay minerals with the sodium, calcium, and magnesium which were present in the coal as ion-exchangeable cations. In many highly fused deposits these complex phases appeared to nucleate from regions of high iron content. Highly sintered and fused deposits contained abundant alkali and alkaline earth aluminosilicates.

The strongest deposits contain abundant crystalline material and the weaker ones do not. Previous work²⁴ has suggested that the formation of crystalline phases, particularly melilites, in addition to a high sodium content is the key to understanding ash deposition. It was suggested that sodium melilite may be the problem-causing species. In the present work it was found that in nearly all cases sodium was not concentrated in the crystalline material but rather was concentrated in the glass adjacent to the crystals. This finding suggests that the sodium-containing liquid which causes extensive viscous flow sintering and dissolution of the other ash components is responsible for the development of deposit strength.

The relative amounts of glass and crystalline phases formed

during sintering is a critical parameter affecting the strength of the deposit. This was deduced from the sintering test in which a reduction in strength of fly ash from bituminous coal heat treated above 1050°C was found to be associated with the formation of a crystalline phase during sintering. The formation of crystals raises the viscosity of the residual liquid and hence retards the rate of the sintering process. Compounds added to promote the crystallization of the glass in the fly ash from bituminous coals reduce the strength of the sintered product. In addition, sintering of fly ash from bituminous coal after the removal of the glass material also gives a weaker sintered product.

The primary factors involved in the formation of strong deposits appear to be the availability of alkali and alkaline earth elements to act as a flux, and temperature. Tests on coals from which the ion-exchangeable cations had been removed produced deposits weaker than those from the untreated coals. Tests on float/sink fractions showed that the fraction containing the highest amount of alkali and alkaline earth elements produced the strongest deposits. Tests performed at a lower hot zone temperature produced weaker deposits than tests with the same coal at higher temperatures. Gas velocity may also have an effect. Preliminary results showed that a weaker deposit was formed at low gas velocities.

The development of deposit strength is primarily due to

viscous flow sintering with a reactive liquid phase. The liquid phase consists of low-melting alkali and alkaline earth aluminosilicates. Crystallization very likely changes the composition of the melt and the viscosity of the remaining liquid phase. Deposit strengths show an inverse relationship with viscosity consistent with the theory of development of deposit strength.¹⁴ The quantity of liquid predicted (by equilibrium thermodynamic calculations) to form at 1300°C correlated well with deposit strength.

Since glass material appears to promote viscous flow sintering in the deposit a reduction in viscosity of the glass enhances the sintering. This was illustrated in the sintering of fly ash from bituminous coal in a reducing atmosphere which developed higher strength at lower temperature than comparable tests in air. This behavior is probably due to the iron being reduced to Fe^{+2} , which entered the glassy network to form a lower melting point iron-glass phase, enabling sintering to take place. Synthetic coal containing illite formed a very strong deposit, and is another example to illustrate the importance of a low melting point glass which promotes the viscous flow sintering process at a relatively low temperature.

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