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FUNDAMENTAL STUDIES OF THE MECHANISMS OF SLAG
DEPOSIT FORMATION

Topical Technical Report

Studies on Initiation, Growth and Sintering in the Formation of Utility
Boiler Deposits

By
Malee Tangsathitkulchai
Leonard G. Austin

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Studies on Initiation, Growth and Sintering
in the Formation of Utility Boiler Deposits

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ABSTRACT

Three laboratory-scale devices were utilized to investigate the mechanisms of the initiation, growth and sintering process involved in the formation of boiler deposits. Sticking apparatus investigations were conducted to study deposit initiation by comparing the adhesion behavior of the ash drops on four types of steel-based heat exchanger materials under the conditions found in a utility boiler and an entrained slagging gasifier. In addition, the adhesion behavior of the ash drops on a reduced steel surface were investigated. All the ash drops studied in this investigation were produced from bituminous coals.

A vertical externally-heated tube furnace was used as an accelerated test to study the deposits formed from nine coals, ranging from high-rank bituminous coals to low-rank subbituminous and lignite coals, under conditions simulating a utility boiler. Synthetic coals prepared from known minerals dispersed in a copolymer (polyester-styrene-divinyl benzene) were also tested to obtain a clearer understanding of the behavior of the minerals in coals during the deposit formation process.

The development of deposit strength by fly ash sintering was investigated to provide an insight into the process of sintering occurring in the deposit mass. The investigation was accomplished by measuring the physical and chemical changes of the sintered products as a function of temperature. Additional parameters studied were the composition, time and atmosphere.

The combined use of these three techniques to evaluate deposit initiation, growth and sintering established a preliminary hypothesis to explain the mechanisms of utility boiler deposit formation.

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SUMMARY

A sticking test was used to study the adhesion of molten drops of coal ash, formed by melting a small pellet of ash in a hot flame, where a drop falls and freezes onto a pretreated substrate held at a controlled temperature. Investigations of the adhesion behavior of molten ash drops from three bituminous coals on four types of steel-based material (T-11 mild steel, 304 SS stainless steel, plasma-sprayed aluminum coated steel and alonized steel), gave the following conclusions.

Slag drops on an oxide layer on T-11 steel under oxidizing conditions appeared to be compatible with the layer and tended to give strong adherence. The logarithmic increase of strength of adhesion with increasing substrate temperature was the typical adherence behavior of slag drops on oxidized steel. Cross-sections of interfaces between slag drops and the oxidized surface of T-11 steel showed that there was a strong fusion of the drop to the oxide layer, which produced high thermal stresses and subsequent cracking in the drop upon cooling to room temperature.

The weak adhesion of the slag drop on a reduced steel surface supported the hypothesis that strong adhesion occurs as a result of chemical compatability between the slag drop and an oxide layer, and is not a result of mechanical anchoring in microporosity of the steel surface.

The T-11 steel with sulfiding pretreatment showed a weakly adherent sulfided layer. Slag drops contacting this substrate under

reducing conditions appeared less compatible than on oxidized layers and there was no large increase in strength with increasing substrate temperature, although weak adherence did occur at relatively low temperatures ($\sim 200^{\circ}\text{C}$). This was due to adhesion to the surface sulfided layer with fracture via detachment of this layer from the underlying steel. The cross-section of the interface between slag drop and the sulfided surface of T-11 steel showed no strong fusion of the drop to the sulfide layer; consequently, cooling produced no thermal stress and no cracking of the drop.

The oxide film on 304 SS stainless steel appeared to be much thinner, with a less spongy structure, than that on T-11 steel. The sticking of slag drops on this substrate occurred at higher substrate temperature than for T-11 steel. Cross-sectioning of the interface between a slag drop and the oxidized surface of this material showed a similar appearance to that of T-11 steel.

The sulfided plasma-sprayed aluminum coating on T-11 steel was not significantly different in appearance from the surface of this substrate under oxidizing conditions, indicating resistance to attack by sulfur-containing gas. The coating prevented very strong sticking, but appeared to soften enough to give a weak adherence, under both oxidizing and reducing conditions. Cross-sectioning results of adherence of slag drops on this substrate in both environmental conditions exhibited a definite aluminum layer on the substrate with clear evidence of softening of this layer under the drop, but no strong fusion of the drop to the layer.

The alonized T-11 steel surface appeared to resist oxidation or sulfidization. This is presumably due to the presence of the alloy (Al/Fe) on the surface. Cross-sectioning results for both oxidizing and reducing conditions exhibited no strong fusion of the drops to the alonized surface. It was concluded that the alonized T-11 surface was superior (in resisting the formation of a strongly adherent initial layer of slag drops) to 304 SS stainless steel which was superior to T-11 steel, especially under reducing conditions. The plasma-sprayed aluminum coated surface did not appear from the sticking test to be a feasible substrate, because of the softening of the top layer of this surface.

A comparison of the dependence of adhesion to the composition of the slag drops was not possible in the present investigation because it was observed that the temperature of the tested drops prior to being dropped on the substrate were not be the same for different ashes. Since the adhesion is strongly affected by the initial temperature of the drop, this introduces an uncontrolled variable when comparing results from one ash or mineral to another.

A vertical, externally-heated, luminar flow tube furnace was used to study the deposits formed from nine coals, ranging from high-rank coals (bituminous) to low-rank coals (subbituminous and lignite), under conditions simulating the formation of fly ash in a utility boiler. Entrained pulverized coal in a primary air stream was injected into the furnace and preheated secondary air entered through a flow straightener. Solution of the fluid dynamic equations under test conditions showed that a uniform blending between the two streams occurred with a laminar velocity profile and this kept the burning

particles in a thin ray in the center of the furnace with no collision with the furnace walls. The gas stream and central ray of fly ash were accelerated by a constrictor prior to impingement on the substrate, which was held at a controlled temperature simulating a boiler steel heat transfer surface.

The results obtained from this furnace were as follows. The test gas temperature of 1300°C through the constrictor is at the upper level of temperatures at the exit of a radiant section of a utility boiler furnace, and it led to a rapid growth of deposit on the substrate held at 500°C. A coal rate of one-third of a gram per minute for 30 minutes gave deposits from 0.3 to 3 cm in height, depending on coal type; these deposits could be mounted in resin, cross-sectioned and analyzed.

The deposits had structures, growth lines, and chemistry similar to those reported for full-scale boiler wall deposits, with strong sintering and fusion occurring at the top of the deposit which is the region exposed to the highest gas temperature. The deposits contained little sodium and sulfur (which are found in convective pass deposits in boilers) because of the short particle residence times of 1-2 seconds and the high gas temperature at the point of deposition.

Expression of the rate of deposit growth in terms of the variation of ash sticking coefficient with time showed the marked differences in behavior between different coals and between low and high rank coals. Under these extreme conditions the ash sticking coefficient approached 1 for some high-rank coals, at the top of deposit for a thick deposit. Severely slagging coals showed a strongly accelerated rate of deposit growth, whereas less severely slagging coals showed a more uniform rate of deposition.

Under these testing conditions in this laboratory furnace, it may be hypothesized that different coals have different sticking coefficients because of the following possibilities: (1) the proportion of approaching fly ash particles which are molten, or solid but sticky, are different for different coals; (2) the size distribution and density of fly ash particles produced from different coals are different; and (3) the physical and chemical characteristics of the deposit mass formed from different coals are different due to the differences in the subsequent sintering, chemical reaction and melting behaviors of the particles after deposition, thus leading to different capture probabilities for fly ash striking the deposit.

It has not yet been proven that the vertical laminar flow tube furnace test is a correct simulation of combustion and deposition in a utility boiler. However, the results can be used to deduce a preliminary hypothesis for the mechanics of the formation of deposit in this type of laboratory furnace which may have features in common with full-scale practice. The qualitative model for deposition is as follows. The fly ash and the flue gas stream accelerate as they pass through the constrictor, and a thin vertical ray of gas and particles strikes the substrate and changes direction sharply to flow radially over the substrate and leave around the edges. The average size of ash particles in the deposit mass is large compared to that of the dust material deposited around the deposit mass, indicating that the ash particles forming the deposit mass reach the deposit by an initial impaction mechanism, whereas the smaller dust particles tend to follow a streamline of the flue gases and deposit by a particle-diffusion mechanism (Brownian and/or thermophoresis). The deposit forming at the

center of the substrate has, therefore, the typical physical appearance of a cone or a mountain growing towards the direction of the incoming hot gases.

The initiation of deposit is by the adherence of molten ash droplets to the oxide layer of the substrate. On striking the cool substrate, ash droplets solidify rapidly and only a small fraction of the droplets adhere with sufficient strength to the oxide layer to remain in place. Several small islands of adhered hemispherical particles form and these create more roughness for further deposition. The fraction of ash droplets that form the initial layer of the deposit from high-rank coals is rich in Fe and that for the deposit from low-rank coals is rich in both Fe and Ca.

Following the initial layer of deposit, ash accumulation to form a massive deposit depends on particle-to-particle adherence as the deposit grows. Although some of the incoming fly ash particles impact onto the particles of the initial layer of deposit, it is possible that a major fraction of the adhered fly ash particles are simply trapped by the rough surface created by the initial layer. As the deposition proceeds, this lower portion of deposit is eventually buried underneath a more sintered deposit mass which builds up from the hotter surface of the upper layers of deposit. The lower portion of deposit is insulated by the upper layers of the growing deposit, and subsequently exists as a loose and slightly sintered layer due to the low temperature in this region.

The following growth mechanism is clear: as the deposit grows towards the incoming hot gases the top of the mass becomes hotter as it builds up and collisions of fly ash with a sticky deposit result in more sticking. When the deposit reaches a certain height, the top of the deposit can give virtually complete capture of the fly ash (sticking coefficient = 1). However, as the deposit grows toward the constrictor, the presence of the deposit spreads the flow of gas so that not all the particles strike the top of the deposit. In addition, the presence of sufficient liquid in the top of the deposit may allow material to be detached from the top by the impact of the gas.

Preliminary results of tests using synthetic coals (polymer-mineral mixtures) showed that the deposits produced are similar in morphology to deposits produced from coals. The tests using synthetic coals containing pyrite, clays, and quartz showed that the presence of volatile or condensed alkali species was not necessary for deposit formation, at least under the conditions used in these tests.

Synthetic coals containing pyrite or pyrite plus clays formed strong initial deposit layers as well as giving a substantial build-up of deposit. On the other hand, synthetic coal containing illite grew a deposit but did not involve a strong initiating layer.

The deposit from a synthetic coal containing pyrite, clays, quartz and calcite gave a structure and chemistry similar to that from an actual coal with the same mineral composition. This showed the role of calcite, which appears to act as a flux to allow the fusion of pyrite, clays and quartz during combustion.

Synthetic coal containing quartz did not give melting of the quartz thus did not form a deposit. On the other hand, it may be hypothesized that if quartz were present in a close association with fluxing species in the same particles during combustion, it might form low melting silicate fly ash particles and subsequently form a deposit. In addition, quartz particles may be trapped in the deposit mass formed by other, sticky, particles and subsequently be assimilated in the deposit.

The temperature gradient in the deposit mass causes the process of sintering, chemical reaction and melting to occur at different rates at different locations in the deposit. Development of deposit strength by fly ash sintering was thus investigated in this study to provide an insight into the process of sintering. The test method consisted of heating a small ash pellet and following the development of strength as a function of temperature and time in either an oxidizing or a reducing atmosphere, to simulate the local conditions at different locations in a deposit. The physical (sintered strength and shrinkage) and chemical property changes of the sintered products were measured. The Raask electrical sinter point of a fly ash was also determined, that is, the electrical resistance across the fly ash pellet was measured and the sharp change in electrical properties at a certain temperature defines the electrical sinter point, since it indicates the formation of the liquid which leads to sintering.

Results from the sintering investigation of fly ash from a high-rank coal (Upper Freeport) indicated that viscous flow sintering was promoted by a glass material in the spherical fly ash particles, resulting in a large increase in strength with increased sintering

temperature and a higher amount of bonding glassy phase, so that the shapes of the initial spherical fly ash particles were no longer distinguishable. This is essentially similar to the sintering occurring in the upper regions of the deposit in the laminar flow tube furnace from high-rank coals, where temperatures are 800 - 1200°C. In the higher part of this temperature range (1050°C-1200°C), there were phase decomposition and chemical reactions that accompanied or preceded the sintering process. These removed some of liquid bonding phase and produced solid crystalline phases (mainly mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$). The crystalline phases did not readily dissolve into the liquid and their amounts increased with temperature, resulting in a rise of the viscosity of the residual liquid and a reduction in the rate of sintering and development of strength.

Results from the sintering test using fly ash from low-rank coal (Beulah lignite), on the other hand, exhibited a small increase in strength with temperature due to chemical reactions which quickly transform the glass material in the fly ash into the crystalline phase. This is not surprising, since the bulk composition of the fly ash suggests that many crystalline phases such as gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) as predicted by the phase diagram are likely to occur already at the sintering temperatures of 800°C - 1200°C. The interlocking of crystal bridges and the associated sintering provided a considerable strength to the matrix but still much lower than the strength of the sintering of fly ash from high-rank coal containing bonding glass.

The sintering behavior of fly ash from high-rank coal, described above involved a viscous flow mechanism of the bonding glassy phases

that formed from the glass material in the as-received fly ash. A very weak sintered product was observed when the glass material was extracted from the Upper Freeport fly ash using a diluted HF solution prior to sintering. The relative amounts of glass and crystalline materials was, therefore, a critical parameter affecting the strength of deposit: the higher the glass content the stronger the deposit. However, there are several types of species that can be associated with the glasses and it had not been determined which glass contributed most to forming a strong deposit. To identify these species, various silicate glass compounds containing sodium, calcium and iron in the pulverized form were added to the fly ash prior to sintering, and their sintered products were investigated giving the results summarized as follows. The addition of calcium silicate and sodium silicate (glass compounds) into a fly ash from high-rank coal enhanced the sintering rate at the lower temperatures ($<1000^{\circ}\text{C}$). At the higher temperatures ($>1000^{\circ}\text{C}$), however, calcium and sodium species devitrified the glass bonding phase to form the crystalline phases which result in a reduction in strength. However, sodium species do not as readily devitrify the associated glass to form a crystalline phase in comparison to the calcium species. It is concluded that sodium-based glass in the fly ash particles contributes to viscous flow sintering, and remains mainly as glass during cooling thus forming a stronger deposit. Calcium-based glass, on the other hand, becomes involved in the formation of crystalline phases, thus forming a weaker deposit at sintering temperatures greater than 1000°C .

Added iron-based glass (iron silicate) did not affect the sintering behavior and strength of the deposit. This indicates that

the fly ash probably already contained sufficient iron-based glass necessary for sintering and formation of a strong deposit. The greater amount of iron-based glass in fly ash (formed from pyrite in close association with clays) may lead to a high slagging tendency and a greater deposit removal problem.

Iron is responsible for initiating and enhancing the sintering rate at lower temperatures in a reducing atmosphere as compared to those in air. The iron in the reduced state readily entered into the glassy network to form a lower melting point iron based glass, thus enabling sintering to take place.

The sintering mechanism of a mineral mixture was quite similar to that of the fly ash with the same mineral composition, except that the sintering of the mineral mixture occurred at higher temperatures ($>1000^{\circ}\text{C}$). The sintering in this case depended on the rate of glass phase formation, which required a higher temperature and longer time to produce a sufficient amount of glass phase necessary for initiating and developing strength.

The results of sinter point determinations using the ash electrical resistance method showed that the onset of sintering was due to the presence of a liquid phase from the lowest melting point component in fly ash, and not due to any increase in sinter necks. A fly ash with a low sinter point, which indicates sintering at lower temperatures, did not necessarily produce a strong deposit. This is true when there are chemical reactions which remove the bonding phase necessary for the sintering process, so that the resulting deposit may be brittle and easy to remove by sootblower operation.

Chapter 1

INTRODUCTION

1.1 Background and Statement of Problem

Coal has been the main source of energy for generating electricity in the United States and its utilization will still be growing for the coming century. The predominant mode of coal utilization in utility boilers is pulverized coal combustion. Pulverized coal fired boilers are generally designed for volumetric heat release rates which give high temperature to the steam entering the turbine and hence a high generation efficiency. However, inorganic constituents associated with coal are converted to ash and vapors during coal combustion and can form deposits in the boiler, and this problem is aggravated by high temperatures of the pulverized coal flame (1500-1650°C). To put into perspective the large amount of ash formed in a 1000 megawatt power plant burning coal, a plant burning about 400 tons per hour of a pulverized coal containing 10 percent ash produces about 40 tons of ash per hour. The ash forms bottom ash and slag, fly ash, and some fractions may form deposits on heat transfer surfaces inside the boiler.

As a consequence of ash deposition, the heat transfer from the flame to the surfaces transferring heat to water and 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 contained in the deposits. Large deposits in the upper furnace area can break away

from the wall tubes by their own weights, 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 more scientific investigation on 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 the increasing energy demands. This investigation contributes to a clearer understanding of deposit formation process in utility boilers.

Some new trends in advanced coal technologies are not free from the ash deposition problems. For instance, entrained slagging gasifiers are prime candidates for use in advanced Coal Gasification Combined Cycle power plants. Recovery of sensible heat from the raw synthesis gas product of entrained slagging gasifiers is required to make them more economically attractive. However, during the cooling process, ash particles can deposit on the heat exchanger surfaces. The deleterious effects of the ash deposition give such problems as reduction of heat exchanger efficiency, corrosion, and premature failure of the system. Little is known about the mechanisms of ash deposition on the heat exchanger surfaces under the reducing environment in entrained slagging gasifiers and this creates new incentives for further ash deposition research.

The process of ash deposit formation is very complicated and complex in character. A complete understanding of this process includes fundamental data on 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 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 reaction, 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 deposit formation process are not only coal related but also strongly dependent on the boiler configuration and operational conditions. As a consequence, a precise and quantitative knowledge of ash deposit formation mechanisms has not yet been obtained.

There has been a considerable amount of work performed to explain the initiation and growth of ash deposits and it appears that the sintered strength of 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 in character. The fly ash formed is a heterogeneous material and the sintering process is often accompanied or preceded by a

specific chemical reaction involving certain inorganic constituents in a particular fly ash particle. Within the ash deposit, the process of sintering and chemical reactions proceed at different rates at different locations depending on the local temperature-time history. In addition, there are many factors such as ash particle shape, 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, the relatively few investigations which have been made have resulted in insufficient information to understand the mechanisms responsible for the ash sintering involved in the boiler deposit formation process.

1.2 Scope of Investigation

There are three interconnected laboratory tests used by the Fuel Science Program of the Pennsylvania State University to obtain a clearer fundamental understanding of the mechanisms of initiation, growth, and sintering of ash deposits. These tests are: (1) the Sticking Test; (2) the Vertical Externally-Heated Tube Furnace Test; and (3) the Shrinkage-Electrical Resistance Sintering Test. The techniques and the several conclusions from their previous use are summarized in Chapters 3, 4, and 5. The scope of this thesis falls into three parts based on the use of these three tests.

(1) The sticking test was used to study slag-steel interaction involved in the initiation process of deposit formation in utility boilers. It consists of melting a small ash pellet, which is then dropped onto a temperature controlled steel surface and the adhesion

force between the solidified ash drop and the steel surface determined. Preliminary results of the adhesion force of the ash drops adhered to four types of steel-based materials under the conditions found in a utility boiler and an entrained slagging gasifier were previously reported by Abbott (1984). However, the information on the adhesion force alone was not sufficient to fully explain the adhesion behavior. As an extension of that work sticking apparatus investigations were conducted in the present study to obtain information on the morphology and chemistries at the interface between the ash drop adhered on the steel-based substrate under the similar conditions used in the previous study. This was performed by repeating some of the tests to provide samples for mounting in resin followed by vertical cross-sectioning. This exposes the interface between the ash drop adhered on the substrate which can then be examined. Sticking apparatus was also utilized to investigate the adhesion behavior of ash drop on a reduced steel surface. The purpose was to verify a hypothesis that it was necessary for the steel substrate to have an oxide layer in order for a molten ash drop to adhere on solidifying.

Three low temperature ashes from three bituminous coals, and a synthetic gasifier slag were tested on four potential heat exchanger materials (steel-based substrates) in an air and a typical medium BTU gasifier environment. A pyrite and a pyrite plus kaolinite mixture were also tested on the steel-based materials in air. The investigations to study the adhesion behavior of these coal ashes and minerals on the steel-based heat exchanger materials could lead to a better understanding of the components and conditions that contribute

most to the formation of strong initial deposit layer and eventually lead to the formation of troublesome deposit. The morphology and chemistries at the interface of the ash drop adhered on the steel-based substrate were analyzed using a scanning electron microscope (SEM), a SEM equipped with energy dispersive spectrometry (SEM-EDS) and an automated SEM-EDS point-to-point analysis.

(2) The vertical externally-heated tube furnace test was previously constructed to overcome some of the inherent limitations of the sticking test (Abbott and Austin, 1984). This test uses a small amount of pulverized coal (~50 gm) which is burned and passed, in a thin stream, down a tube heated to simulate the temperature-time history of a pulverized coal flame. The fly ash formed is then impacted on an oxidized steel substrate held at a controlled temperature, and the initial deposit layer examined. The present study was aimed to investigate the mechanisms of ash deposit formation relevant to boiler deposits. This approach required some modifications of the previous vertical externally-heated tube furnace test to enable the growth of sufficient deposit so that the course of the deposition could be studied. The type of ash responsible for the deposition was examined from the initial ash layer at the oxidized steel boiler tube surface to the last surface of deposit next to the flame side. For this reason, the previous procedure and conditions of the furnace were adapted with modifications to permit sufficient growth of adherent deposit which could be weighed, vertically cross-sectioned, and examined in a variety of ways. The expression of the rate of growth in terms of the variation of ash sticking coefficient with time was also used to characterize the way the

deposit grows. In addition, operating conditions were varied and the amount, structure and composition of deposits were analysed to identify the conditions and components that contribute most to the deposition process. This could lead to a better prediction of the potential deposition behavior of a coal and an appropriated action taken to minimize deposition, e.g., selectively the coal or operating the boiler at conditions which inhibit deposit formation.

Nine coals covering the range from high-rank coals (bituminous) to low-rank coals (subbituminous and lignite) were studied to obtain and compare the deposit formation behavior between these coals using the vertical externally-heated tube furnace apparatus. In addition, synthetic coals prepared from known minerals dispersed in a polymer were also investigated to obtain a clearer understanding of the behavior of the minerals in coals during the deposit formation process. Comparative morphology and chemistry were examined at various locations in the deposits using, SEM, SEM-EDS and X-ray diffraction (XRD) analysis. Mounting and vertical cross-sectioning of the deposit adhered on the oxide steel surface was also performed and examined using an optical microscope and SEM-EDS analysis.

(3) It is known that there are differences in physical properties and chemical phases between an initial deposit material and an aged deposit, due to sintering and chemical reaction occurring over a wide range of temperature and time within the boiler deposit. Although the shrinkage-electrical resistance sintering test utilized in the previous study gave useful information, such as the temperature at which ash begins to sinter, the operational conditions are not suitable to obtain information on the physical and chemical changes

occurring over the considerable range of temperature and time that an ash actually undergoes within the deposit (Conn, 1984). For this reason, a new sintering test was devised in the present study. The approach was to sinter fly ash pellets as a function of temperature, time, and under either an oxidizing or a reducing atmosphere to simulate the local conditions at different locations within the deposit. Subsequently, the study of fly ash sintering was facilitated by (1) measuring property changes of the sintering products, including sintered strength using an Instron compressive strength and morphology using SEM; and (2) ascertaining the chemical changes of the sintered products using XRD analysis.

Sintering behavior for three fly ashes from high-rank coals (bituminous) and a fly ash from a low-rank coal (lignite) were investigated in this study. The purpose of these tests was to understand the sintering behavior of fly ashes from these various types of compositions of coals. This may help to establish the mechanism of fly ash sintering. In addition, the behavior of these fly ashes during laboratory sintering were compared with their known performance in utility boilers to assure the potential of this laboratory test in the application to the real boilers. Tests were performed to identify the low melting point components that promoted the sintering and how they behave in the sintering of fly ash, by either adding of low melting point compounds such as glass, glass-forming material and alkali compound into the fly ash or extracting of low melting point components from fly ash. Model materials such as a soda-lime-silica glass (soda glass) and alumina mixture, and mineral mixtures, were also studied to obtain a clearer

understanding of the sintering behavior of glass and minerals. This information was correlated to the composition of the original fly ash with respect to its sintering behavior. An Instron compressive strength apparatus was utilized to determine the sintered strength of sintered products. The morphology of sintered products were studied using SEM. XRD analysis was performed to identify the phases contained in the as-received fly ash and the sintered products.

Chapter 2

BACKGROUND INFORMATION AND LITERATURE REVIEW

2.1 A Pulverized Coal Fired Boiler

2.1.1 Boiler Configuration and Operating Conditions

Figure 2.1 is a schematic configuration of a typical Radiant boiler for pulverized coal. The Radiant boiler derives its name from the fact that the absorption of a heat transfer surface is largely by radiation. The system incorporates the following essential features: coal storage and pulverization; coal and air supply to the burners; ignition, combustion and radiant zones of heat transfer surfaces in the furnace (waterwall, radiant superheater and reheater tubes); bottom ash removal equipment; on-line tube cleaning facilities (sootblowers); steam drum; superheater and reheater tube banks for convective heat transfer; economizer; air heater; fly ash removal equipment; fans; and stack.

The pulverized coal (normally 80% passing through 75 μm aperture sieve) and primary air mixture is injected into the furnace via burners, where turbulent mixing with the secondary air occurs. The coal is suspended as a cloud of small particles in the combustion air and when the pulverized coal particles are subjected to a very high heating rate (10^5 to 10^6 $^{\circ}\text{C}$ per second) in the flame, there is a loss of moisture followed by the evolution of volatiles (devolatilization). As the thermal decomposition continues, ignition and subsequent combustion of the volatiles occur. The temperature range over which this occurs and the quantity of volatiles involved depend on the nature of the coal. The heat generated by the

Figure 2.1. Outline of a typical Radiant boiler for pulverized coal with opposite wall firing; dots indicate sootblowers; $T_1 = 1500-1700^{\circ}\text{C}$; $T_2 = 400-450^{\circ}\text{C}$; $T_3 = 1200-1400^{\circ}\text{C}$; $T_4 = 600-650^{\circ}\text{C}$; $T_5 = 1000-1200^{\circ}\text{C}$; and $T_6 = 800^{\circ}\text{C}$.

combustion of the volatiles is then transferred back to the coal particle from the flame envelope surrounding it, causing further devolatilization of the coal at higher temperature. During this stage, combustion of the evolved volatiles and of the residual char may overlap, provided that oxygen can gain access to the surface of the char particles. As the devolatilization is nearly completed, heterogeneous char combustion (solid-gas reaction) dominates the burning of the residual char until the particle is completely burnt. Efficient mixing of the burning pulverized coal particles and the combustion air is essential. In addition, particles should have sufficient residence time in the high temperature zone to facilitate burnout.

A temperature of 1500°C to 1750°C is obtained in the radiant section of the furnace depending on the coal and process conditions. Heat generated in the combustion process appears as furnace radiation and sensible heat in the products of combustion. The equation of energy balance for a steady operation of a utility boiler is given by,

$$Q = q_r + q_s \quad (2.1)$$

where Q , q_r and q_s are, respectively, the rate at which heat energy is released in the combustion chamber, absorbed by furnace wall tubes, and passes out of the furnace as the heat content of the flue gas and fly ash. Waterwall tubes surrounding the flame remove a substantial fraction of the heat from the flame, with heat transfer to the waterwalls being principally by radiation. The metal temperature of the waterwall tubes is maintained at about 400°C to 450°C by water circulation within the tube. At the lower part of the furnace, the metal temperatures of the waterwall tubes are lowest and become higher

as the water rises in the tubes. The flow of water and steam mixture passes through the riser tubes into the steam drum where the steam is separated from the mixture and passes to superheater tubes. The cooler flue gases ($\sim 1100-1400^{\circ}\text{C}$) leaving the top of the furnace contact a bank of superheater tubes which contains flowing steam, and a combination of radiative and convective heat transfer to the tubes further heats the steam before it enters the high-pressure turbines. The cool steam is returned from the high-pressure turbines and reheated in the reheater tubes and transported to the low-pressure turbines thus increasing efficiency. The metal temperature of the superheater and reheater tubes may be maintained as high as 650°C since high temperature is required to superheat the steam. The steam is condensed after the turbine and the water is transported to the economizer which extracts heat from the flue gases (800°C) and the heat is transferred to the condensed water before recycling to the furnace. The economizer also preheated the feed water before entering to the furnace, thus it helps to improve turbine efficiency. The flue gases from the economizer enters the air heater where the final heat extraction occurs. The air heater has two important and concomitant functions: it cools the flue gases before they pass to the atmosphere; at the same time it raises the temperature of the incoming air of combustion thereby increasing the coal-firing efficiency.

Turbine efficiencies are highest when the temperature of the steam entering the turbine is as high as possible. This is possible by positioning the steam superheater tubes closer to direct radiation from the flame. However, the metal tubes may be damaged when exposed to too high temperature and too high concentration of corrosive

constituents (alkali and sulfur) in the flue gases. The ash produced during combustion is another major problem since it accumulates on the tubes causing increased resistance to heat transfer and a loss of efficiency.

There are two major types of ash deposits occurring in a utility boiler. Accumulation of ash deposits on the furnace walls and other surfaces that are exposed predominantly to the radiant heat transfer section is known as slagging. Slag deposits typically consist of an outer layer of molten phase and an inner layer of sintered or semifused phase. Fouling is the accumulation of ash deposits on convective heat exchange surfaces such as superheaters and reheaters at gas temperatures below the melting point of the bulk ash. Fouling deposits are usually associated with a strong sintered phase and possibly a semifused phase at the outer layer.

2.1.2 Heat Transfer through a Boiler Deposit

At the high temperatures in the pulverized coal fired furnace ($1500-1750^{\circ}\text{C}$), radiation is the primary mechanism of heat transfer from the hot combustion products to the waterwall tubes. The heat given up by the furnace combustion products, which results in the generation of water and steam mixture within the waterwall tubes, must pass through a series of resistances: those of the boundary layers of gases; the stagnant gas film adjacent to the deposit; the ash deposit on the tube surfaces; the tube walls; the internal scale deposited by water evaporation; and the water and steam boundary layer (Foxwell, 1958, and Singer, 1981). Figure 2.2(a) illustrates the temperature gradient resulting from the flow of heat through some of these series

(a)

(b)

Figure 2.2. Temperature gradient (a) across furnace wall tube and deposit exposed to radiant heat transfer region; and (b) across superheater tube and deposit exposed to convective heat transfer region; diagram is not the actual scale (Raask, 1985a).

of resistances for waterwall tubes exposed to radiant heat, with deposit accumulation (Raask, 1985a).

At high temperatures in the furnace, heat is transferred through the boundary layers of gases and the stagnant film of gas mainly by radiation. Having transferred through the stagnant gas film, the heat is conducted through the layer of ash deposit. As a result of poor heat conductance of the deposit material in comparison to that of the boiler tube, a steep temperature gradient is also set up across the deposit layer. The heat then passes on through the boiler tube that is made up of a thin layer of iron oxide layer, a poor conductor, and a steel, a good conductor, and then meets the third poorly conducting layer that consists of scale before passing into water where boiling and conversion into steam takes place.

The heat transfer from the hot combustion products through the superheater and reheater tubes in the convective region is also passed through a similar series of resistance as that of the waterwall tubes described above. However, radiation is less important in this region and the superheater and reheater tube metal temperature is higher but the thermal gradient and the maximum temperature of the deposit with the same thickness are lower as compared to those of the waterwall tubes (see Figure 2.2(b)).

As mentioned above, ash deposit on the metal boiler tubes can be considered as an insulating material and thus has a dominant role in reducing the heat transfer from the flame and hot gases to the water and steam flowing in the tubes. Heat flow q_r through a layer of deposit is given by,

$$q_r = \frac{k}{x} A (T_s - T_c) \quad (2.2)$$

where T_s is the temperature of the hot face of deposit layer, T_c is the temperature of the cold face of the deposit layer, k is the effective thermal conductivity of the porous ash material, A is the area of surface involved in heat transfer, and x is thickness of deposit material. The overall heat transfer through the deposit having the temperature at the outer surface of deposit as T_s and the metal tube fluid temperature T_w is given by,

$$q_r = U A (T_s - T_w) \quad (2.3)$$

where U is the overall heat transfer coefficient. Boiler deposits may exist as loose dust on cooled metal tube surface (initial layer), a succeeding sintered matrix and a fused material at the outer layer of the deposit. These layers exhibit different thermal conductivities since the bulk density of initial, unsintered deposit may be between 500-600 kg/m³, whereas that of the sintered and fused ash may be as high as 2200 kg/m³ (Raask, 1985b). It is therefore, necessary that the properties of the deposit at different layers should be taken to be account if accurate results are needed. The heat transfer should be treated as the heat flows through a wall that is made up of various layers of deposit thickness, $x_1, x_2, \dots$ and the effective thermal conductivity of different layers of deposit, $k_1, k_2, \dots$. Subsequently the overall heat transfer coefficient, U , can be expressed in the form,

$$U = \left[\left(\frac{x_1}{k_1} + \frac{x_2}{k_2} + \dots \right) + \frac{x_0}{k_0} + \frac{x_m}{k_m} + \frac{1}{h} \right]^{-1} \quad (2.4)$$

where x_0, k_0 are thickness and thermal conductivity of the iron oxide layer respectively, x_m, k_m , are thickness and thermal conductivity of the metal tube, respectively, and h is coefficient of convective heat

transfer from the tube to water and steam.

2.2 Physical and Chemical Properties of Coal Ash

The physical and chemical properties of coal ash formed from coal combustion play critical roles in determining the potential of a coal to contribute to deposit formation in boilers. Therefore it is important to consider the composition and mode of occurrence of the inorganic constituents in coal, and the reaction pathways relating the properties of inorganic constituents in coal to those in ash and deposits. These aspects will be briefly considered as follows.

The term inorganic constituents usually applies to all inorganic matter in the coal (mineralogical components) and includes those inorganic elements which may occur in organic combination. Table 2.1(a) illustrates the most common minerals identified in coals, which are given with the decomposition temperature or melting point. Tables 2.1(b), 2.1(c), 2.1(d) and 2.1(e) show inorganic constituents of selected high-rank and low-rank coals. In general, the average ash composition of a low-rank coal is higher in the alkali and alkali earth elements but lower in silica and alumina. A major portion of the inorganic constituents in low-rank coals are often present as exchangeable cations associated with carboxylic functionalities and are associated with the mineralogical components to a lesser extent (Jenkins, 1984). The exchangeable inorganic species are normally dispersed throughout the coal matrix, which is a significant difference from the other mineralogical components in coals. On the other hand, the percentages of inorganic constituents associated with the organic portion in high-rank coals are typically low as most of

Table 2.1(a). Common minerals identified in coal.

Mineral	Chemical formula	Melting point, °C
<u>Clay minerals</u>		
kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	} mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (1810)
muskovite	$\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	
illite	$(\text{Fe}, \text{Ca}, \text{K})_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	
montmorillonite	$(1-x)\text{Al}_2\text{O}_3 \cdot x(\text{MgO}, \text{Na}_2\text{O}) \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$	
<u>Oxide minerals</u>		
quartz	SiO_2	1710
hematite	Fe_2O_3	1567
magnetite	Fe_3O_4	1592
rutile	TiO_2	1827
<u>Carbonate minerals</u>		
calcite	CaCO_3	927*
dolomite	$\text{CaCO}_3 \cdot \text{MgCO}_3$	777*
ankerite	$\text{CaCO}_3 \cdot \text{FeCO}_3$	727*
siderite	FeCO_3	527*
<u>Sulfide minerals</u>		
pyrite, marcasite	FeS_2	1027 [@] , 1567 ⁺
chalcopyrite	CuFeS	1027
galena	PbS	1097
<u>Sulfate minerals</u>		
barytes	BaSO_4	1582
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1452
kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	1122
thenardite	Na_2SO_4	884
melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	482*
<u>Chloride minerals</u>		
halite	NaCl	800
sylvite	KCl	770
<u>Phosphate mineral</u>		
apatite	$\text{Ca}_5\text{F}(\text{PO})_4$	1227

*denotes the decomposition temperature under 1 atmosphere of CO_2 or SO_2 as appropriate; @ rapid heating rate and in the absence of air; + slow heating rate and in the presence of air; source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 2.1(b). Chemical composition of high temperature ash (ASTM) from some selected high-rank coals.*

Coal	Illinois # 6	Pittsburgh # 8	Upper Freeport
Rank	High-volatile Bituminous	High-volatile Bituminous	Medium-volatile Bituminous
Seam/Mine/ Location	River King Mine, Peabody Seam, Ill.	Champion Plant, Pa.	Upper Freeport Seam, Keystone Power Plant, Pa.

Weight percent of equivalent oxides

SiO_2	48.3	51.1	54.1
Al_2O_3	17.5	26.9	25.9
TiO_2	0.8	0.9	1.3
Fe_2O_3	20.9	15.2	9.6
CaO	4.7	0.9	1.7
MgO	0.9	0.6	1.0
K_2O	1.6	2.2	2.9
Na_2O	0.6	0.2	0.3
P_2O_5	0.2	0.1	0.3
SO_3	4.6	0.7	1.1
Ash	22.3	10.0	18.1

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

Table 2.1(c). Chemical composition of high temperature ash (ASTM) from some selected low-rank Coals.*

Coal	Powder River Basin	Texas	North Dakota
Rank	Subbituminous	Lignite	Lignite
Seam/Mine/ Location	Powder River Basin, Wy.	Wilcox Formation, Tx.	Beulah-Zap Seam, Nd.
Weight percent of equivalent oxides			
SiO ₂	25.8	48.7	18.7
Al ₂ O ₃	15.1	18.6	8.7
TiO ₂	0.8	1.2	0.5
Fe ₂ O ₃	7.4	5.6	13.4
CaO	24.7	9.1	18.9
MgO	5.5	2.1	5.4
K ₂ O	0.3	0.9	0.1
Na ₂ O	1.6	0.3	9.5
P ₂ O ₅	0.4	0.0	0.4
SO ₃	18.2	11.4	21.4
Ash	7.9	21.5	11.5

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

Table 2.1(d). Mineralogical composition of low temperature ash from some selected high-rank coals.*

Coal	Illinois # 6	Pittsburgh # 8	Upper Freeport
Rank	High-volatile Bituminous	High-volatile Bituminous	Medium-volatile Bituminous
Seam/Mine/ Location	River King Mine, Peabody Seam, Ill.	Champion Plant, Pa.	Upper Freeport Seam, Keystone Power Plant, Pa.
<u>Mineral (wt.%)</u>			
quartz	25	23	25
pyrite	29	27	10
calcite	2-5	n.d.	n.d.
gypsum	n.d.	n.d.	5
kaolinite	5	25	30
illite + mixed layer clays	35 [@]	10 [@]	20 [@]
Ash	22.0	11.8	21.6

n.d. = not detected; @ = estimated value; * Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

Table 2.1(e). Mineralogical composition of low temperature ash from some selected low-rank coals.*

Coal	Powder River Basin	Texas	North Dakota
Rank	Subbituminous	Lignite	Lignite
Seam/Mine/ Location	Powder River Basin, Wy.	Wilcox Formation, Tx.	Beulah-Zap Seam, Nd.
<u>Mineral (wt.%)</u>			
quartz	15	20-25	12
pyrite	n.d.	1-5	5
calcite	2	n.d.	5
gypsum/bassinite ⁺	25	15-30	20
kaolinite	15	30-35	n.d.
iron sulfate	n.d.	n.d.	10 [@]
Ash	9.7	23.7	14.6

⁺bassinite is often an artifact of the low temperature ash when ashing low-rank coals; @ = estimated value; * Source = Mineral Constitution Laboratories, The Pennsylvania State University, Pa.

them are contained in the mineral forms.

The general behavior of inorganic constituents during coal combustion is illustrated in Figure 2.3 (France et al., 1984). The figure depicts the combustion of a 50 μm diameter coal particle with 1 μm inorganic inclusions. As combustion proceeds, the inorganic constituents are converted to ash residue and vapors, with each product having different pathways. The unvaporized ash disintegrates, forming submicron size beads that are left on the surface of the char particle. When the temperature of the char particle is sufficiently high to fuse the ash, these submicron size beads of ash may either remain as discrete droplets or coalesce into larger droplets on the non-wetting surface of the coke (Raask, 1985d). The vaporized inorganic matter may nucleate homogeneously, forming particulates in the 0.1 μm range, and partly condenses on the unvaporized ash particles in the flue gases. Fly ash particles entrained in the combustion gases of pulverized coal fired boilers are generally spherical showing that melting of the ash particles takes place. However, there are some large particles of quartz (>50 μm) that do not fuse completely (Raask, 1969). A portion of the ash particles may also form hollow spheres (cenospheres) due to gas evolution during rapid heating of mineral components in char particles in the pulverized coal fired flame.

Evidence exists that, on the whole, each coal particle burns separately without many collisions between particles so that inorganic constituents of each coal particle transformed to ash having its own particular composition (Sarofim et al., 1977). The melting temperatures of some pure inorganic constituents in coals normally

Figure 2.3. Behavior of mineral matter during pulverized coal combustion (France et al., 1984).

exceed the flame temperature encountered during combustion. However, interactions between various inorganic components within each coal particle occur and result in a wide variety of compounds having lower melting temperatures than that of the original inorganic constituents. Therefore some of the fused spherical ash particles form as a result of the fluxing action between the components associated within each coal particle. Some minerals such as illite and biotite that contain small amount of fluxing elements (Fe, Ca, Na, K) in their structures appear to be an exception, forming low melting point glassy spheres at temperatures well below the flame temperature (Bryers, 1984).

At temperatures above about 500°C and at a very high heating rate (10^5 to 10^6°C per second) pyrite and marcasite decompose to pyrrhotite and sulfur. These species ultimately oxidize to iron and sulfur oxides in the presence of excess air. The carbonates such as calcite, dolomite, and siderite decompose losing carbon dioxide to form the respective oxides at temperatures over 700°C to 900°C . Gypsum dissociates into calcium oxide and sulfur oxides at about 1500°C . These basic oxides are available for subsequent interactions with acidic oxides derived from quartz and clays in the same coal particle.

Clays such as kaolinite, illite, montmorillonite, and biotite when heated to about 500°C lose their hydroxyl groups. With removal of the hydroxyl groups, the clay structure partially collapses, retaining only some degree of order. This results in a more open structure, and thus allows clays to easily react with other associated fluxing species such as alkali, alkaline earth and iron compounds to form complex aluminosilicates at temperature higher than 900°C . When deficient in these fluxing species, the three dimensional

aluminosilicate layer structure of clay transforms with the loss of amorphous silica to a spinel type compound ($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$). A further heating to 1100°C the spinel loses SiO_2 to transform into mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). However, if the cooling rate is rapid, clays simply pass into amorphous glassy phase without crystallizing to spinel or mullite.

At room temperature quartz is known as low temperature quartz (α -quartz) and at temperature of 573°C it goes through a transformation with no breaking of bonds to form high temperature quartz (β -quartz). β -quartz transforms to tridymite at 867°C which transforms to cristobalite at 1470°C . However, these transformations are very sluggish and, unless heated very slowly, quartz simply passes into a viscous silica glass at 1500°C to 1600°C . When cooling from the liquid state, silica has a great tendency to assume a glassy condition without crystallizing. The silica glassy structure is less dense than the crystalline phase, and hence is capable of combining with basic oxides such as Na_2O , CaO , FeO , Fe_3O_4 , and Fe_2O_3 to form low melting point silicates.

In the later stages of particle combustion, organically bound elements such as sulfur and alkali are vaporized (Reid, 1981). The organic sulfur is released into the combustion gases as sulfur dioxide and some subsequently forms sulfur trioxide. Some researchers proposed that during combustion localized reducing areas occur within the coal particle which promote rupture of the tetrahedral bond in quartz and aluminosilicates which will react with the volatilized sodium to form sodium silicates or complex sodium aluminosilicates (Johnson and Litter, 1963, and Taylor, 1974). This possibly accounts

for the retention of a significant fraction of volatilized sodium. The remainder is present as sulfate fume particles in the flue gases and may condense on the cooled ash particles and on the cooled tubes downstream in the boiler.

In a large pulverized coal fired boiler, the physical and chemical environments vary greatly within a furnace: it passes from reducing conditions while organic matter is present to a stage where ash is in contact with carbon, to oxidizing conditions as the carbon burns out. In addition, the time-temperature history of each particle is unlikely to be the same in such a large flame. These factors together with the wide range of heterogeneous assemblage of the organic and inorganic constituents in each coal particle, further complicate the behavior of inorganic constituents during coal combustion. Clearly, there can be a wide range of the physical and chemical properties of the resultant fly ash particles that generally determine whether they will adhere to heat transfer surfaces and subsequently form deposits.

As determined by x-ray diffraction analysis, fly ash largely consists of amorphous or glass material and specific crystalline materials. The major glass material in fly ash form primarily as a result of thermal transformation of glass forming minerals such as clays and quartz in the coal flame. The properties of resultant glass in the fly ash are not only related to the glass formers, but are also strongly dependent on the availability of fluxing elements (Na, K, Ca, and Fe), the capture of volatilized sodium, the time-temperature history, the oxidizing and reducing atmosphere, and the rate of cooling of the ash particle.

According to the Random Network Model, glasses consist of cation and anion units and are viewed as a three dimensional networks or arrays, lacking symmetry and periodicity, as shown in Figure 2.4(b) (Kingery et al., 1976). Glasses are approximately characterized by the main broad background ($2\theta = 15-30^\circ$) in the x-ray diffraction pattern due to the non-repeating structure of glass units at regular intervals. Bockris et al. suggested that the glassy units are in the form of a polymer with mixtures of chains and rings depending on the nature and concentration of the cations (Brockris et al., 1955). The highly charged cation having high ionic potential (Si^{+4}) (see Table 2.2) is a network former that forms coordination by linking with oxygen anions. Quartz, for example, is a good glass former due to the fact that all corners in its tetrahedral structure are shared and the oxygen is linked to two Si^{+4} cations in the silica glassy network. Clay minerals such as kaolinite, montmorillonite, and illite have at least three out of four corners in their structures shared and are also a good glass former known as aluminosilicate glass.

The low ionic potential cations such as alkali (Na^+ and K^+) and alkaline earth (Ca^{+2}) are network modifiers. The effect of adding these cations into a glass is viewed as the introduction of additional oxygen ions which are capable of breaking up the glass network. As more oxygen ions become available, chains in the polymer can terminate more frequently or the polymer average size becomes smaller. This means that the three dimensional glassy network is partially broken by the network modifiers and transformed to a lower melting point glass as compared to the original glass (see Figure 2.5). If the concentration of these network modifiers is great, the effect of

Figure 2.4. Schematic representation of (a) ordered crystalline form; and (b) random-network glassy form of the same composition (Kingery et al., 1976).

Figure 2.5. Schematic representation of the structure of a sodium silicate glass (Kingery et al., 1976).

Table 2.2. Ionic potentials of various species (values calculated from the ratio of oxidation state to cation radius) (Vorres, 1979).

Species	Cation radii (Å)	Ionic potential (Å) ⁻¹
Si ⁺⁴	0.42	9.5
Al ⁺³	0.51	5.9
Ti ⁺⁴	0.68	5.9
Fe ⁺³	0.64	4.7
Mg ⁺²	0.67	3.0
Fe ⁺²	0.74	2.7
Ca ⁺²	0.99	2.0
Na ⁺	0.94	1.1
K ⁺	1.33	0.8

adding these species into the glass readily breaks up the glass network, eventually leading to crystallization (devitrification).

The ferrous and ferric ions (Fe^{+2} and Fe^{+3}) have lower ionic potentials than the network formers but higher than the network modifiers, so they are referred to as network intermediates. The ferrous ion has significantly lower ionic potential ($\text{Fe}^{+2} = 2.7 \text{ } \frac{\text{eV}}{\text{\AA}}$), thus it can be viewed as a better network modifier as compared to the ferric ion ($\text{Fe}^{+3} = 4.7 \text{ } \frac{\text{eV}}{\text{\AA}}$). Iron readily interchanges between the +2 and +3 valency states depending on the oxygen partial pressure of the atmosphere and is a critical component affecting the nature of fly ash. In a reducing atmosphere, the ferrous ion in association with a glass may cause a partial break-up in the glassy network, resulting in transformation to a lower melting point glass. In contrast, the ferric ion in an oxidizing atmosphere in association with a glass may not change the properties of the glass.

As mentioned earlier, the average mineral composition of a high-rank coal, in general, is high in clays and quartz. The temperature of mineral particles in the pulverized coal flame normally exceeds 1500°C , and it is therefore expected that all clays and quartz particles (with the exception of large quartz) form glass. If the concentration of pyrite in a high-rank coal was high, and if the glass formers were closely associated with pyrite, most of the glass formed primarily from clays and quartz may be present in the fly ash as a low melting point glass, due to fluxing action of iron. Low-rank coals, on the other hand, are generally lower in clays and quartz, and their alkalis (Na, K) and Ca contents are higher. The Na, K, and Ca are generally highly dispersed in low-rank coals, and therefore have a

great possibility of being closely associated with clays and quartz. Thus, the likelihood of having a high fraction of low melting point glass material in fly ash is at least as great as for high-rank coals. Since glass is a major component in fly ash, and can be sticky if not frozen, it can adhere strongly to heat transfer surfaces and subsequently form a strong deposit.

2.3 Ash Deposit Formation Process

2.3.1 Ash Deposit Formation Mechanisms

The formation of an ash deposit on heat transfer surfaces in pulverized coal fired boilers can be explained in physical and chemical terms by the following sequence of events:

- . Fly ash formation and transportation towards the heat transfer tubes;
- . Initial adhesion of ash particles onto the heat transfer tubes and further deposit build up (the sticking process);
- . Interactions between the deposited ash particles to form a strong deposit matrix (the sintering process).

In the first stage, the transport of ash particles from the high temperature flue gas onto the tubes takes place either by inertial impaction or diffusion, depending mainly on the size and mass of ash particles, flue gas velocity and the aerodynamic conditions of the heating surfaces (France et al., 1984). In the first case, due to the larger kinetic energy of large ash particles, they may leave the streamlines and impact on the tube surfaces encountered. These impacting particles have an increased probability of adhesion because the kinetic energy of the particle is transformed to heat upon impact,

possibly allowing more sticking behavior. In the second case, the small ash particles and vapors move toward the tube surface by Brownian motion, by turbulent diffusion, or by thermodiffusion through the temperature gradient in boundary layer, and subsequently form deposits on the tube surface.

The transfer of the ash particles to the heating surfaces by itself does not mean formation of a deposit if the particles are not retained on the tube surface after the collision. The influence of the slag-steel interaction is determined by the physical and chemical properties of the ash particles and the tubes, the temperature level, and the conditions of the flue gas flow around the tubes. With all other parameters being equal, sticky or molten particles obviously 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 formation of the solid phase. This process may also occur on the surfaces of the silicate 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.

Burner and wall slags occur at the lower part of the furnace where the metal temperatures of the waterwall tubes are lowest (the tube temperatures become higher as the water rises in the tubes). 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 the molten ash particles to the wall as liquid droplets. It has been demonstrated that 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) which gives sticking and slag initiation at relatively low metal temperatures (Abbott, 1984). If a thick deposit occurs on the tubes in this region, the layer of slag next to the metal tube will be of a frozen solid and the layer of slag next to the flame can be liquid. Jones et al. quantitatively examined microstructure of a boiler wall slag using electron microprobe analysis technique (Jones et al., 1985). They reported that the slag region adjacent to the furnace wall consisted primarily of a glassy phase layer having high porosity and the slag region near the flame side contained a high proportion of crystalline phases and less porosity. 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.

The upper part of the furnace is exposed to lower flue gas temperature than the lower part of the furnace and the ash droplets have cooled sufficiently so that they should not deposit on the tubes at this region. However, upper wall slags have existed and have been found to be enriched in certain fractions of the coal ash. Presumably their origin is the result of the different low melting inorganic components in the ash particles differing from the mean ash composition. According to Bryers and Walchuk, deposition of iron rich ash particles occurs mainly by the inertial impaction process in the upper wall regions. This was determined in a pilot-scale furnace fired with high-rank bituminous coals (Bryers and Walchuk, 1983). With this finding it was proposed that the mechanism of the upper wall slag formation appeared to be the selective deposition of specific inorganic species.

Although iron was identified as an inorganic constituent in high-rank bituminous coals that contributes most to form a strong and troublesome deposit, iron content alone can not successfully be used to assess the coal slagging tendency. The mode and distribution of iron and other associated inorganic constituents in coal, and the physical and chemical environments in the boilers, must also be known. On the other hand, for low-rank coals that have low iron content, the slagging mechanism may not be similar to that of the high-rank coals.

The mechanism involved in the formation of fouling deposits has been the subject of considerable investigations. There is evidence that the initiating and bonding agents are mainly alkalis (especially sodium) and sulfate fumes that condense on the tubes and possibly on the cooler fly ash spheres before deposition. Fouling deposits are usually called bonded deposits, since they often exist as an aggregate of dry ash particles bonded together by a liquid phase that has subsequently frozen. Sodium sulfate and calcium sulfate are detected as the bonding substances in the bonded deposit formed from high-sodium low-rank coals (Rindt et al., 1983). For high-calcium low-rank coals calcium sulfate is the bonding substance (Dimitrue and Ilmar, 1980). In the inner layer of the deposits next to the tubes, high concentrations of alkali and sulfur were always found. This phenomenon was believed to be the result of a migration of a fraction of alkali sulfates through the deposit to the tube by thermal diffusion. This inner layer enriched in alkali sulfates can cause corrosion and tube thinning in the convective section of the boilers (Raask, 1985e).

2.3.2 Methods of Studies for Ash Deposit Formation Process

Experimental study of the ash deposit formation process has been performed using apparatus of sizes ranging from full-scale utility boiler units down to small laboratory-scale apparatus. There have been a few investigations that obtained information on ash deposition behavior by examining chemical, physical and thermal properties of deposits collected from the full-scale utility boiler units (Jackson and Jones, 1983, and Rindt et al., 1983). However, the study of deposit mechanisms in a full-scale unit is often not feasible because of the cost and difficulties of obtaining suitable measurements. Smaller units and pilot-scale boiler units are designed to simulate as closely as possible a full-scale unit operation (Honea, 1983, Bryers and Walchuk, 1983, Hein, 1983, Jackson et al., 1983). These smaller units offer the advantage of lower testing cost as compared to that of the full-scale utility boiler units. However, ash deposition behavior is not only coal related, but also highly dependent on boiler configuration and operating conditions. Thus, the information gathered from smaller-scale units may not always perfectly simulate that of the full-scale utility boilers.

Studies of the mechanisms of deposit formation using the pilot-scale units have led to various proposed models of slagging and fouling. However, the pilot-scale units appear to be unsuitable for either verifying the proposed mechanisms or for fundamental investigations. In the few investigations using pilot-scale units that have been made, inconclusive results on the mechanisms of deposition and the properties of deposits were obtained because the physical and chemical parameters such as gas velocity, particle size

distribution, particle time-temperature history were difficult to control and determine over the duration of the test. As a consequence, a simple, flexible and rapid laboratory test is urgently needed to examine deposition. A possible method has been introduced recently as a vertical tube furnace (Wall and Wibberley, 1983, and Abbott and Austin, 1984). With this type of apparatus, particles of pulverized coal, ash and selected compounds are dropped and passed through an externally-heated tube region in which boiler conditions are simulated, and the ashes and deposits are then characterized.

There are several interconnected laboratory techniques that give information on ash deposit formation processes. For instance, the study of bonding of fly ash particles to boiler steel surfaces to initiate deposit formation can be performed using the sticking test (Moza and Austin, 1979). In this technique, an ash droplet is dropped onto an oxidized boiler steel surface held at a controlled temperature corresponding to that of the heat transfer tubes of a utility boiler. The contact angle and adhesion force of the fly ash droplet to the boiler steel surface are subsequently determined. The drops were found to stick to the surface of oxidized steel at a temperature similar to that of boiler wall tubes (400°C - 500°C). The results from this type of test gave similar wetting and adhesion behavior as that of a pilot-scale pulverized coal combustor (Austin, Abbott, and Kinneman, 1983). The sticking test provides useful information although the test conditions do not closely simulate the conditions in a utility boiler.

Further deposit build-up and development of strength (sintering) have been a subject for several investigators. These

phenomena depend on the behavior of ash particles adhered upon a deposit already present. This process depends on the local conditions such as time, temperature and atmosphere. The background information and literature review on these processes are given in the sections 2.4 and 2.5.

The study of the chemical relationship between deposited ash particles and the original inorganic constituents in pulverized coal is another line of research. Developments in this approach have been primarily due to application of more sophisticated analytical methods for investigating the chemical composition of an ash deposit and the inorganic constituents in coal on a microscale basis. For example, a computer-controlled SEM-X-ray fluorescence analysis technique has been developed for quantitative analysis of individual mineral grains or coal particles (Lebiedzki et al., 1973, Long, 1973, Huggins et al., 1982, Moza et al., 1983, and Gomez, 1985). This approach may be a useful way of examining the ash deposition problem since the problem is not likely to be related only to the behavior of inorganic constituents in coal or ash on an average basis, but rather originates from the behavior of individual particles, whose compositions can be very different from the average value. Each fly ash particle has its own melting, sticking, and sintering behavior. Thus, examination of the composition of pulverized coal and the corresponding fly ash and deposited ash on a particle by particle basis may permit an investigation to identify the inorganic constituents and compositions that contribute most to the formation of strong and troublesome deposit, so that the expected severity of the deposition problem for a given coal can be estimated and verified.

2.4 Sintering Processes in an Ash Deposit

2.4.1 Brief Review of Sintering Theory

Sintering is defined as the heat treatment of a system of individual particles or of a porous body, with or without the application of external pressure, in which some or all of the properties of the system are changed, resulting in the reduction of the free energy in the direction of those of the porosity-free system (Thummler and Thomma, 1967). In this section, a brief description of the theory of sintering without the application of pressure is presented.

Three stages of sintering have been defined. In the initial stage, necks form at points of interparticle contact and usually but not always the particle centers approach each other. The relative amounts of neck growth and shrinkage that take place depend upon the mass transport mechanisms that are operative. In the intermediate stage, the particles can no longer be distinguished but the pores continue to form a more or less connected phase throughout the compact. Eventually the pores become isolated from each other, giving the final stage.

Since the sintering phenomena can occur with or without the presence of a liquid phase, the sintering process can be classified as either solid state or liquid phase sintering, with each process having different time and temperature dependencies.

In a solid state sintering process, the free energy difference between the surface of a particle and the neck areas between particles results in a driving force for material to transfer. Matter can migrate from the particle surface, from the particle bulk, or from

grain boundaries between particles by surface, lattice, or grain boundary diffusion (see Figure 2.6). The transfer of material from the surface to the neck by surface diffusion does not lead to any decrease in the distance between particle centers, that is, this process does not result in shrinkage of the powder compact and a decrease in porosity. Studies have shown that of the many diffusion paths available, surface diffusion is the most important during the early stage of solid state sintering, with grain boundary diffusion and volume diffusion becoming subsequently more important (Burke, 1962, Kuczynski, 1972, and Coble, 1973). Mass transfer results in a change in the distribution of pore size along with a reduction in the overall porosity and an increase in mechanical strength.

Kingery developed a mathematical model for the first stage of the solid state sintering process based on a diffusion control mechanism, giving

$$\frac{x}{r} = \left[\frac{K D \gamma \Omega}{k T} \right]^{1/5} r^{-3/5} t^{1/5} \quad (2.5)$$

(Kingery et al., 1976). In this equation x is the neck radius and r is the radius of particles, D is the self-diffusion coefficient, γ is the surface tension, Ω is the atomic volume of the solid, k is the Boltzmann constant, T is the absolute temperature, and K is a constant dependent upon pore geometry. The shrinkage of this compact is then expressed as:

$$\frac{\Delta L}{L_0} = \left[\frac{K D \gamma \Omega}{k T} \right]^{2/5} r^{-6/5} t^{2/5} \quad (2.6)$$

where L_0 is the initial length of the pellet and L is the length at time t .

Mechanism Number	Transport Path	Source of Matter	Sink of Matter	Shrinkage
1	Surface diffusion	Surface	Neck	No
2	Lattice diffusion	Surface	Neck	No
3	Vapor transport	Surface	Neck	No
4	Boundary diffusion	Grain boundary	Neck	Yes
5	Lattice diffusion	Grain boundary	Neck	Yes
6	Lattice diffusion	Dislocations	Neck	Yes

Figure 2.6. Alternate paths for matter transport during the initial stages of sintering (Kingery et al., 1976).

From this model, it can be seen that particle size r is the critical control variable since the sintering rate is roughly proportional to the inverse of the particle size; as the particle size is decreased, the rate of sintering is raised. The other variable is the diffusion coefficient which is affected by the composition and by the temperature. Sintering time is not the major variable in the process since just merely sintering for long periods does not cause extensive solid state sintering due to the low power of time dependence.

The neck growth relation (equation 2.5) is obviously relevant only to the initial stage of sintering. Theories concerned with the intermediate and the final stages are more difficult to quantify, particularly because of the difficulties introduced by grain growth (Greskovich and Lay, 1972). In addition, there has been difficulty in relating the values of the constant K to the geometry of a real compact that had been sintered to the later stages of sintering (Coble, 1961, and Johnson, 1970).

When a liquid phase is present in the sintering process, different considerations apply. There are two types of liquid phase sintering, depending on the properties of the liquid phase involved in the process. These are sintering with a reactive liquid phase and sintering with a non-reactive liquid phase (Burke and Rosolowski, 1973, and Kingery et al., 1976). Both types of liquid phase sintering have a viscous flow mechanism in the initial stage of sintering, but they have different mechanisms in the later stages of sintering.

In the initial stage of liquid phase sintering, the liquid on each particles exerts a traction tending to pull them together. The

result is that the particles rearrange by sliding, so as to reduce the porosity by improving their packing. If the quantity of liquid present is great, or if it wets the solids well, then most of the particles are completely covered leaving the pores bound by the liquid. The driving force for sintering arises from the surface tension of liquid on the pore surfaces, which tends to collapse the pores. The sintering at this stage proceeds by a viscous flow process and may result in a pore-free material if the amount of liquid present is sufficient to fill all of the original porosity.

In sintering with a reactive liquid phase the solid is to some degree soluble in the liquid, and sintering will continue to proceed rapidly at the end of the first rearrangement process described above. In this case, matter is transported from particle to particle by diffusion through the liquid. The mechanism of mass transport is that of dissolution and reprecipitation, with the driving force arising from increasing solubility of a portion of the solid surface with decreasing radius of curvature of the particles. This results in the shrinkage of the small particles and the growth of the larger ones, as well as the disappearance of all sharp corners, which produces a characteristic structure of rounded coalesced grains surrounded by a liquid. Sintering at this stage proceeds rapidly, because of the high diffusion coefficient of mass transfer in the liquid.

In sintering with a non-reactive liquid phase there is little or no solubility of the solid in the liquid at the conclusion of the initial stage and sintering will proceed in a manner similar to that which would occur if no liquid were present. The sintering rate in this case is much slower than the rate in the case where sintering

occurs with a reactive liquid phase as described above, but is faster than for solid state sintering because viscous flow is operative in the initial stage of sintering.

The sintering of soda-lime-silica glass (soda glass) is the most extensively studied ceramic systems used to illustrate the viscous flow mechanism. Soda glass is regarded as a homogeneous material which sinters by a viscous flow mechanism at temperatures near 600°C (Kuczynski., 1949, and Kingery et al., 1976). In the soda glass system, sintering proceeds with the aid of a viscous liquid phase formed at the sintering temperature. The liquid solidifies to form glass on cooling and serves as a bond to provide mechanical strength to the matrix.

The viscous flow is defined by the equation:

$$f = \eta \epsilon \quad (2.7)$$

where ϵ is the strain rate, f is the acting stress, and η is the viscosity coefficient. Stress is required for viscous flow to occur. The stress developed during glass sintering is produced by surface tension. In essence viscous flow is an activated process and the temperature (T) variation of viscosity can be described by an Arrhenius type equation:

$$\eta = A \exp (-E/RT) \quad (2.8)$$

where A is a preexponential constant and R is the gas constant. E is referred to as the activation energy for viscous flow.

Frenkel has derived an equation relating the growth of the interface between two spherical particles of soda glass that sinters

by the viscous flow mechanism:

$$\frac{x}{r} = \left[\frac{3 \gamma}{2 \eta \rho} \right]^{1/2} t^{1/2} \quad (2.9)$$

where x is the radius of the interface, r is the original radius of the spheres, γ is the surface tension, η is the viscosity, ρ is the radius of curvature of particle contact, and t is the time (Frenkel, 1949). This equation states that the increase in contact diameter (x^2) is proportional to t . Other important factors are surface tension, viscosity, and particle size. The shrinkage of the heat treated compact is given by:

$$\frac{\Delta L}{L_0} = \frac{3 \gamma t}{4 \eta r} \quad (2.10)$$

where L_0 is the initial length of the compact and L is the length at time t . The Frenkel equation (2.10), predicts that the initial shrinkage of a compact of spherical particles will be linear with time. Since the surface tension is not changed much by composition, whereas viscosity changes greatly with temperature and composition, the most important control variable in this type of sintering is viscosity. For a typical soda glass the viscosity changes by a factor of 1000 over an interval of 100°C (Kingery et al., 1976); the rate of sintering changes by an equal factor over the same temperature range. This means that the temperature must be closely monitored and controlled. In addition, the rate of sintering can be increased by changing the composition to lower the viscosity of the soda glass material.

For liquid phase sintering of a heterogeneous material consisting of many components that are different in melting points, it

is the low melting point components that initiate and enable viscous flow sintering to occur. However, there may be some chemical reactions that concurrently occur during the heat treatment process. The presence of any new reaction product in the system complicates the analysis of the sintering mechanism. The simplified equations describing sintering by a viscous flow mechanism cannot readily be applied to the sintering of heterogeneous material in this case because the quantity of liquid phase, the composition of the liquid, and the viscosity of the liquid all depend on temperature and chemical composition of the components in the powder compact.

2.4.2 Laboratory Coal Ash Sintering Tests

Although the sintering process of fly ash to form a strong deposit is quite complicated, several laboratory methods have been developed to evaluate specifically the sintering characteristics of coal ashes. Most of the studies have determined the rate of sintering for cases where measurements are based directly on Frenkel's viscous flow model. Kuczynski carried out a sintering study by a neck growth measurement technique (Kuczynski, 1949). A spherical glass particle was placed on the surface of a glass slab of the same composition and then introduced into a preheated furnace. It was kept at a constant temperature (600°C) in air or in a gas mixture for a period of 5 minutes to several hours. The radius of the sinter neck between the glass particle and the glass slab was measured microscopically at the ambient temperature. The ratio of x/r (neck growth) was used as a measure of degree of sintering: the higher the x/r ratio, the greater the extent of sintering.

Raask reported some results of the sintering of coal ash particles based on a similar technique (Raask, 1973). The coal ash particles were specifically made homogeneous and spherical by passing ground fused boiler slag through a vertical furnace. Two spherical particles of slag (60 μm in diameter) were sintered at a constant temperature in air. The time for a firm degree of sintering ($x/r = 0.1$) was 135 sec. and 70 sec. at 1100°C and 1150°C , respectively. From these measurements the time required for a given degree of sintering can be calculated for the ash particles of different sizes (using equation 2.9) for a given viscosity of 10^8 N s m^{-2} and a surface tension of fused ash of 0.32 N m^{-1} . The ratio of x/r was used as an indication of four arbitrary stages of sintering of ash deposit on boilers tubes, leading from the initial contact between the particles ($x/r = 0.001$) to the formation of fused slag where the shape of initial constituent particles was no longer distinguishable ($x/r = 0.3$). However, the measurement of neck growth between spherical particles demonstrated the validity of Frenkel's model only for homogeneous material. Therefore, this technique is not suitable for routine testing of sintering characteristics of fly ash because fly ash is a heterogeneous material.

Sintering generally results in a shrinkage of the external dimensions of a powder compact. Smith used a dilatometric shrinkage technique to determine the sinter point of coal ash (Smith, 1956). The sinter point is defined as the temperature at which an ash compact begins to shrink as a result of particle to particle bonding. This measurement gives useful information, and the results can be related to the degree of sintering as in the neck growth technique. With some

coal ashes, however, anomalous results can be obtained when the shrinkage measurement shows no change even though significant sintering has taken place. Deviation in the sintering behavior from Frenkel's model indicated that viscous flow may not be the only process that contributes to the sintering of coal ash.

Raask developed a laboratory method for simultaneously measuring the electrical conductance and the dilatometric shrinkage (Raask, 1982). These measurements are based on the formation of particle to particle bonding leading to enhanced conductance and increased density (shrinkage) of ash compacts. For most of the coal ashes tested there was a concurrent shrinkage of the ash sample and a decrease in the temperature coefficient of electrical conductance at the sinter point temperature. For some coal ashes of high sodium content, however, the sinter point indicated by the conductance measurement was lower than that deduced from the shrinkage measurement. This result illustrates the sintering behavior of ashes that appear to consist of the high melting point component (infusible constituent) and the low melting point component (fusible constituent). Since the conductance technique measures ionic, possibly sodium, mobility, and hence it is a more sensitive method of monitoring the development of sinter bonding than the shrinkage technique. In addition, an unusual sintering behavior was observed as indicated by a rise and fall of conductance with temperature. Raask attributed this phenomenon to the formation of crystalline phase, resulting in a reduction of sodium ion concentration necessary for ionic conduction in the liquid in the sintered matrix present at high temperatures.

Conn reported results on sintering of high temperature ASTM ash, fly ash, and model materials (soda glass and synthetic mineral mixture) based on the Raask method (Conn and Austin, 1984). The technique was modified to measure the ash shrinkage and electrical resistance simultaneously. The sinter point was defined as the temperature at which either shrinkage or a change in electrical resistance occurred, due to increase in particle to particle contact. Most coal ashes showed both simultaneous shrinkage and a change in the relationship between electrical resistance and temperature at the sinter point. However, coal ashes high in alkali often revealed a lower sinter point by electrical resistance measurement. Increasing the alkali oxide or glassy content of a coal ash also appeared to lower the sinter point, probably due to the formation of a liquid phase on the surface of particles. The extent of sintering was observed to increase as a function of temperature and time, with temperature having greater effect.

Stallman and Neavel reported a simple method to assess the sintering propensity of different ashes (Stallman and Neaval, 1980). The sintered ashes were tested in a typical gasification atmosphere (CO , CO_2 , H_2 , H_2S , and H_2O). The ash was sieved before heat treatment and sieved again after cooling. The weight percentage retained on a 100-mesh sieve was used as an indication of degree of agglomeration or sintering. The initial agglomeration occurred as a result of bonding by low melting sulfides (FeS , CaS and NaS) formed during the heat treatment process. It was noted that the rate of agglomeration increased rapidly with temperature corresponding to Frenkel's viscous flow model. However, the degree of ash agglomeration did not change

with time. The deviation from Frenkel's viscous flow model clearly demonstrated a secondary phenomena, possibly due to phase decomposition and chemical reactions that occurred during the sintering process.

Several investigators have used compressive strength measurements as a measure of ash fouling tendency. The method was developed by Barnhart and Williams (Barnhart and Williams, 1956). They used fly ashes from operating boilers firing bituminous coals. For fouling coals, the development of strength generally occurred at low temperatures ($\sim 700^{\circ}\text{C}$), whereas, in non-fouling coals strength developed at high temperatures ($\sim 900^{\circ}\text{C}$). This method was also used to test the sintered strength of the laboratory ash in order to evaluate ash fouling tendency on a routine basis (Barnhart and Cantieri, 1964). The test has been found to correlate well with fouling on the convective heat exchange surfaces not exposed to the radiant heat, but it has not correlated with sintering in radiant regions of the boiler.

The compressive strength test has been used together with other slagging indexes such as viscosity measurement and high temperature ASTM ash fusion test. Attig and Barnhart used the fly ash from high-rank coals produced from a small laboratory scale pulverized coal combustor, whereas Gibbs utilized laboratory prepared high temperature ASTM ash from high-rank coals in their laboratory tests (Attig and Barnhart, 1963, and Gibbs, 1981). Both groups claimed that the results of sintering strength tests were consistent with the ash fouling and slagging characteristics in large coal fired boilers; however, viscosity and ash fusion tests were not consistent.

Laboratory high temperature ASTM ashes produced from lignitic

coals were tested by Smith et al. using compressive strength measurement (Smith et al., 1982, and Smith et al., 1984). The test predicted greater fouling problems with ashes containing high sodium and lower fouling problems with high calcium ashes. The trend was observed to be consistent with the fouling behavior of the lignitic coals burned in the boilers. In the more recent work, Smith and Szladow found a profound effect of clay related to fouling in a lignite-fired boiler (Smith and Szladow, 1985). They reported that addition of clay to fly ash from lignite significantly increased the ash compressive strength, indicating further aggravation of fouling arising from clay. Lignite ash with a high level of calcium was observed to resist clay fouling. However, once calcium become incorporated in the ash matrix as silicate or aluminosilicate glass upon exposure to high temperature, the capacity of the ash to counteract clay fouling was reduced significantly.

Dering et al. examined the compressive strength of different size fractions of fly ash (Dering et al., 1972). The sintering study of narrow size fractions of fly ash originated from the observation that the smaller ash particles contribute to the formation of bonded deposits in the convective passes as compared with those formed in the radiant region in boilers. They reported that the finest fraction (0-5 μm) of fly ash developed strength at lower temperatures and had higher strength than the larger size fraction from the same coal. This was explained in terms of the increase in the total surface of contact between the particles and the higher concentration of water-soluble alkalis in the finest size fraction of fly ash. These results were observed to be consistent with the tendency of coals to

form a strong bonded deposit in the boilers. In addition, the coals producing the most severe deposits contained the largest quantity of fluxes (Fe_2O_3 , CaO , Na_2O , and K_2O) and had highest concentrations of water soluble alkali in the finest size fraction of fly ash.

The compressive strength of the fine size fraction of fly ash could clearly be used as a measure of fouling tendency of low-rank coals, particularly where there is a significant difference in the water soluble alkali content in the finest size fraction between the coals tested. However, these investigators did not demonstrate a correlation between the compressive strength of the larger size fraction of fly ash and the chemical composition (in particular the iron content) in the coals tested. This additional information could be used to compare the sintering and slagging tendency of coals in the radiant section of the boilers.

The measurement of compressive strength has been employed not only to predict the ash fouling tendency of various coals, but also as a means to evaluate the effect of chemical additives to lower strength of deposits. In using the laboratory compressive strength tests, several investigators reported that addition of a few percent of basic oxides (calcium and magnesium) reduced the sintered strength of fly ashes from low-rank coals (Barnhart and Williams, 1956, Smith and Szladow, 1982, Smith et al., 1984, Engstrom, 1984, and Hazard et al., 1983). Hazard et al. suggested that the additive reacted with some species such as silica and sulfur contained on the surfaces of ash particles, thereby, changing the surface properties of ash particles (Hazard et al., 1983). This appeared to reduce the sintering rate and, hence, gave reduction of the compressive strength.

The laboratory compressive strength test is a good method to evaluate the effect of chemical additives for reducing the deposit strength prior to the use of the additives in a utility boiler. The tested additives should then be introduced to the boiler in the locality where there are the right conditions as determined from the laboratory method. This is, however, difficult to put into practice, thus additives are not widely used in many utility boilers.

2.5 Melting Behavior of Coal Ash and Ash Constituents

As mentioned previously, some of the fly ash particles have lower melting points than that of the average high temperature ash determined in the ash fusion test. If each coal particle forms a sub-system in which the contained inorganic constituents can melt together, almost all possible combinations of low melting conditions can be obtained in at least some of the ash particles. An important guide to the melting behavior of fly ash is the information contained in the phase diagrams both with respect to the formation of molten drops and with respect to the presence of liquid in a sintering mass. A phase diagram can predict both the melting and/or crystallization behavior, under equilibrium conditions of a composition defined by the diagram. Therefore, study of the process of melting undergone by the deposited ash upon exposure to the high temperature may be facilitated by examining the existing phase diagrams of the principal oxide phases such as Al_2O_3 , SiO_2 , FeO , Fe_2O_3 , Na_2O , and CaO .

In theory, phase-equilibrium considerations can yield the lowest temperature at which an ash will be completely liquid (liquidus

temperature), the highest temperature at which the ash will be completely solid (solidus temperature), and the composition and percentages of solid and liquid mixtures at temperatures between the liquidus and the solidus. The formation of low melting point eutectics over relatively narrow ranges of compositions is an important feature in phase diagrams. The first appearance of a liquid will be at the corresponding eutectic temperature and the sample will not be completely liquid until the liquidus temperature is reached (Levin et al., 1964).

The binary phase diagram for the system Al_2O_3 - SiO_2 shown in Figure 2.7 can be represented as the principal oxide phases in an fly ash (an Upper Freeport fly ash produced from a medium volatile bituminous coal from the Upper Freeport Seam, Pa.), for instance, containing SiO_2 53.5 wt.% and Al_2O_3 28.2 wt.%). A liquid phase will develop in mixtures whose compositions are in the range between mullite (72% Al_2O_3) and Al_2O_3 , only at temperatures above 1840°C . Below this temperature, mixtures in this composition range consist of solid mullite and corundum if heated to equilibrium. In mixtures containing less Al_2O_3 than mullite (> 72% Al_2O_3) a liquid forms as temperature exceeds 1590°C . The phases present in such mixtures, at lower temperatures, are solid mullite and either tridymite or cristobalite (SiO_2).

When a third component is added to a binary system, a ternary phase diagram can be used (see Figure 2.8 as an example). The phase diagrams presented here illustrate phase relations over a considerable temperature range, with emphasis on the liquidus region. In such a diagram, heavy lines represent boundary curves separating various

Figure 2.7. Phase diagram for the system Al_2O_3 - SiO_2 (Levin et al., 1964).

phase areas, with arrows indicating directions of decreasing temperatures, heavy lines with crosshatching on one side designate outlines of area within which liquid immiscibility occurs, and light lines represent liquidus isotherms. In order to simplify the complexity of a ternary phase diagram, only the region of which the liquidus temperature equal to 1500°C is drawn in the separated diagram: 1500°C is a typical flame temperature in a pulverized coal flame. In this diagram, the compositions reside within the shade area have the liquidus temperatures lower than 1500°C and those reside outside this area have the liquidus temperatures greater than 1500°C . Example of compositions and the corresponding liquidus temperatures are given in each diagram (see Figures 2.8(b) to 2.10(b)).

Basic oxides such as K_2O , Na_2O , CaO , FeO , Fe_3O_4 , and Fe_2O_3 are known as strong fluxing agents which when added to the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system cause amounts of liquid to form at relatively low temperatures. K_2O has a very strong fluxing effect on $\text{Al}_2\text{O}_3\text{-SiO}_2$ mixtures rich in SiO_2 . The ternary eutectic labelled A in Figure 2.8(a) has a temperature of only 985°C with 10% K_2O addition to the mixture containing 80% SiO_2 and 10% Al_2O_3 . Na_2O has a fluxing action on $\text{Al}_2\text{O}_3\text{-SiO}_2$ mixtures comparable to that of K_2O . The ternary eutectic labelled A in Figure 2.9(a) has a temperature of 1050°C with 9% Na_2O addition to a mixture containing 79% SiO_2 and 12% Al_2O_3 . The phase diagram for the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ is shown in Figure 2.10. It appears that CaO has a moderate fluxing action on $\text{Al}_2\text{O}_3\text{-SiO}_2$ mixtures as compared to that of K_2O and Na_2O . With a 23 % CaO addition to a mixture of 62% SiO_2 and 15% Al_2O_3 , the liquidus temperatures decrease to 1200°C at the ternary eutectic labelled A in Figure 2.10(a).

Figure 2.8(a). Phase diagram for the system $K_2O-Al_2O_3-SiO_2$ (temperature in $^{\circ}C$) (Levin et al., 1963).

Figure 2.8(b). Liquidus curve at 1500°C for the system
 $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$;

Point	% SiO_2	% Al_2O_3	% K_2O	Liquidus temperature, °C
A	50	10	40	1150
B	50	20	30	1500
C	50	30	20	1600

Figure 2.9(a). Phase diagram for the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (temperature in $^{\circ}\text{C}$) (Levin et al., 1963).

Figure 2.9(b). Liquidus curve at 1500°C for the system

$\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$;

Point	% SiO_2	% Al_2O_3	% Na_2O	Liquidus temperature, °C
A	50	20	30	900
B	50	35	15	1500
C	50	45	5	>1500

Figure 2.10(b). Liquidus curve at 1500°C for the system
CaO-Al₂O₃-SiO₂;

Point	%SiO ₂	%Al ₂ O ₃	%CaO	Liquidus temperature, °C
A	50	20	30	1250
B	50	35	15	1500
C	50	40	10	1700

Iron oxides (FeO , Fe_3O_4 , and Fe_2O_3) are also fluxing agents when added to the Al_2O_3 - SiO_2 system. Iron readily interchanges between +2 and +3 valency states depending on the oxygen partial pressure of the atmosphere. In order to evaluate reactions in systems containing Al_2O_3 , SiO_2 , and iron oxides, the oxygen pressure of the atmosphere surrounding the system must be taken into account. Two levels of oxygen pressures, those in contact with metallic iron (reducing atmosphere) and that of air (oxidizing atmosphere), will be used as examples to demonstrate the relations involved. As a visual aid in this discussion, the solidus temperatures for the system iron oxide- Al_2O_3 - SiO_2 in a reducing and an oxidizing atmospheres are shown in Figures 2.11(a) and 2.11(b), respectively. An important difference between the two diagrams (a) and (b) in Figure 2.11 is related to the manner in which iron ions can be accommodated in the structures of mullite and corundum crystalline phases in the system of Al_2O_3 - SiO_2 . Only Fe^{+3} , but not Fe^{+2} , that can accommodate in these crystalline lattices. Hence under the reducing atmosphere even small amounts of Fe^{+2} addition ($\sim 10\%$) will form a liquid phase at 1210°C if the original $\text{Al}_2\text{O}_3/\text{SiO}_2$ mixture contains a high proportion of SiO_2 (see point A in figure 2.11(a)). If, however, the original mixture is high in Al_2O_3 and consists of mullite and corundum, a liquid will not form until a temperature of 1380°C is reached, even after a considerable amount of FeO ($\sim 30\%$) has been added to the mixture (see point B in Figure 2.11(a)). In air, significant amounts of Fe_2O_3 can be absorbed by an Al_2O_3 - SiO_2 mixture that is rich in SiO_2 without forming a liquid phase until the temperature is higher than 1380°C (see point A in Figure 2.11(b)) or higher than 1460°C in the mixture that is rich in Al_2O_3 .

Figure 2.11. Solidus temperatures (as shown in the bracket, °C) for the system iron oxide- Al_2O_3 - SiO_2 in contact with (a) metallic iron (reducing atmosphere) and (b) air (oxidizing atmosphere) (Muan and Osborn, 1963).

(see point B in figure 2.11(b)) (Muan and Osborn, 1963).

The melting behavior of coal ash can be used as a rough guide to the possible behavior in the boiler of inorganic constituents in coal. Several investigators have studied ash melting behavior by constructing ash fusion temperature-composition diagrams for the coal ash (Estep et al., 1934, Estep et al., 1937, Zinzen, 1943, Zinzen, 1944, Barrett, 1947, Dutta et al., 1960, and Dutta et al., 1963). Ash fusion temperature was first determined and then correlated with the chemical composition of the ash (as wt.% oxide). Since coal ash composition varies considerably, and the properties of the ash vary with composition, the melting properties of the ash also varies considerably. Coal ash does not exhibit a sharp melting point, due to its heterogeneity. As ash melts, it first softens and as temperature increases, gradually becomes a viscous liquid. The process is a complex combination of chemical reaction, sintering, and melting. The melting process may differ according to atmosphere, the rate of heating, and the length of time a temperature level is maintained. Some fractions of the ash may tend to melt separately while others may interact. If the major part of the ash approximates the composition of an eutectic, the transition from the first softening to complete melting may occur in a narrow range of temperature. If, however, the ash contains both fusing and refractory components, which do not interact, the melting process may be very gradual over a wide temperature range.

The ash fusion test was initially developed to measure the characteristic deformation temperature of coal ash. It is a tool for measuring and predicting the performance of coals as related to ash

deposit formation in the utility boilers. A coal with a low ash fusion temperature can be expected to give ash deposition problems. The ash fusion test thus has been very valuable in warning designers and operators about such coals. If ash particles arrive at heat transfer surfaces at a temperature below their fusion temperature, they will not form a bonded structure, but instead, will settle out as dust. As such, removal 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 American Society for Testing and Materials (ASTM):D 1857-Fusibility of Coal Ash, provides a standard experimental procedure for determining ash fusion temperature. The test is based on the gradual thermal deformation of a pyramid-shaped laboratory high temperature ASTM ash sample, 3/4 inch in height and 1/4 inch in equilateral-triangular based width. Mounted on a refractory substrate, the sample is heated at a prescribed rate in an electric furnace. A controlled atmosphere (reducing or oxidizing, depending upon the tests to be performed) is maintained inside the furnace. During the heating process, changes in the shape of the pyramid are observed and the following four characteristic deformation temperatures are reported;

(1) Initial Deformation Temperature (IDT): the temperature at which the tip of the ash pyramid begins to show any evidence of deformation. Shrinkage of the cone is ignored if the tip remains sharp.

(2) Softening Temperature (ST): the temperature at which the ash sample has fused into a spherical shape in which the height (H) is equal to the width (W) at the base.

(3) Hemisphere Temperature (HT): the temperature at which the ash sample has fused into a hemispherical shape where the height is equal to a half of the width at the base ($H=1/2W$).

(4) Fluid Temperature (FT): the temperature at which the ash sample has fused down into a nearly flat layer with a maximum height of 1/16 inch.

The softening temperature in reducing atmosphere is referred to as the fusion temperature of an ash, since it has been shown experimentally that the softening temperature is closely related to the liquidus temperature of an equivalent major oxide system (Barrett, 1947).

As mentioned earlier, ash melting behavior has been studied by many investigators by constructing ash fusion temperature-composition diagram for the coal ash system. Some simplifications have been made by neglecting some oxides that have small amounts in the ash components and/or by grouping together those of the oxides having similar fluxing influences on the fusion behavior. However, it has always been realized that the components in ash are not present only as oxides but also in a form of complex mixtures of silicates, and sulfates. Added to this is the fact that slags do not always reach equilibrium in practice, and differences in melting behavior of a component in the presence of others must be taken into account.

Estep et al. considered coal ash as a four component system, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CaO}$ and represented the results by means of cross section through the quaternary prism (Estep et al., 1934). This gave

sets of ternary triangles, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, each representing fixed percentage of CaO (0-8.5%). A typical triangular plot is shown in Figure 2.12(a) where the CaO is 2.6-3.5%. However, the amount of data available was insufficient for the higher levels (>8.5% CaO) contained in some ashes from low-rank coals. Estep et al., therefore, provided the plot of softening temperatures in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CaO}$ system by using the assumption that Fe_2O_3 and CaO are approximately equal in fluxing action on the constituents SiO_2 and Al_2O_3 , as shown in Figure 2.12(b). In a later study, Estep et al. realized that alkalis (sodium and potassium) even at a few percent have a very strong fluxing action in the system of $\text{Al}_2\text{O}_3\text{-SiO}_2$ system and thus should not be ignored. They then proposed that the softening temperature predicted from the four component system ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CaO}$) should be corrected by subtracting 28°C for each percent of the alkali content in the coal ash. This method was later used by Barrett to predict the softening temperature of 178 coal ashes and the results agreed well with the experimental values (Barrett, 1947).

Dutta et al., however, found that the fluxing action of CaO was not constant and varied according to the proportions of the SiO_2 and Al_2O_3 components (Dutta et al., 1960). Therefore, they presented a different set of curves for different $\text{SiO}_2/\text{Al}_2\text{O}_3$ values indicating the variation of the softening temperatures with the percentage of additives (CaO and Fe_2O_3), as shown in Figure 2.13(a). These curves corresponded to the ternary phase diagram of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$, and were plotted on rectangular coordinates for CaO content up to 30% (see Figure 2.13(b)). In their second paper, these authors applied the same method to study the fluxing action of iron in both an oxidizing

Figure 2.12(a). Pseudo-ternary section for the system $\text{SiO}_2\text{-Al}_2\text{O}_3$ at CaO level 2.6-3.5%, temperature in $^{\circ}\text{C}$; small triangle indicates complete ternary diagram showing section actually plotted (Estep et al., 1934).

Figure 2.12(b) Softening temperature ($^{\circ}\text{C}$) isotherms for the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CaO}$; simplified plot, assuming Fe_2O_3 and CaO to be equivalent in action (Estep et al., 1934).

Figure 2.13(a). Softening temperatures, in an oxidizing atmosphere, of ashes and artificial mixtures in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$; corrected for the small content of Fe_2O_3 and alkalis (Dutta et al., 1960).

Figure 2.13(b). Liquidus temperatures in the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (Dutta et al., 1960).

and a reducing atmospheres by representing the results in the forms of two graphs in Figure 2.14 (Dutta et al., 1963). In air, ash fusion temperature of an ash was first determined from Figure 2.13(a) using the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the CaO content of the tested ash. This temperature was then corrected for the alkali content using the method proposed by Estep et al. The value of ash fusion temperature was then plotted with the corresponding Fe_2O_3 content in the tested ash. Each curve shown in Figure 2.14(a) represents a different composition of SiO_2 , Al_2O_3 , CaO, and Fe_2O_3 in which the upper curves corresponds to the lowest ratio of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the lowest CaO content and vice versa. The fluxing effect of iron oxide in reducing atmosphere showed a more rapid decrease in the softening temperature because FeO is a better flux than Fe_2O_3 (see Figure 2.14(b)). It is obvious that the methods of Estep et al. and Dutta et al. are quite reasonable as long as the fluxing action of the neglected oxides and other phases (silicates and sulfates) in the ash are small.

Zinzen grouped together those oxides having similar fluxing influences on the softening temperature, and the results were presented in a ternary phase diagram (Zinzen, 1934, and Zinzen, 1944). The three coordinated axes were: (1) $\text{SiO}_2 + \text{Al}_2\text{O}_3$; (2) $\text{FeO} + \text{Fe}_2\text{O}_3$; and (3) $\text{CaO} + \text{SO}_3 + \text{MgO} + \text{remainder}$. He then divided the diagram into five main regions (a) to (e) according to the difference in fusion behavior and in chemical reactions that accompany or precede the melting of the typical coal ashes with compositions in each of these regions. The diagram was used as a crude guide to explain five types of tested coal ashes which varied in their deposit formation tendencies.

The reactions between mineral-derived phases that lead to the

Figure 2.14(a). Softening temperatures for ashes and artificial mixtures in the system SiO_2 - Al_2O_3 - Fe_2O_3 -CaO-(MgO)-alkali oxides in oxidizing atmosphere (Dutta et al., 1960).

Figure 2.14(b). Softening temperatures for ashes and artificial mixtures in the system SiO_2 - Al_2O_3 - Fe_2O_3 -CaO-(MgO)-alkali oxides in reducing atmosphere (50:50 hydrogen/steam mixture) (Dutta et al., 1960).

melting of coal ash during combustion have been investigated by Huffman and Huggins (Huffman and Huggins, 1983). They illustrated that the assumptions inherent in the high temperature ASTM ash fusion tests were incorrect. Their results showed that the IDT is not the temperature at which the liquid phase first appears. The liquid phase formed as a result of a solid state reaction producing a low melting point compound. The melting behavior of ash was found to correlate closely with the liquidus temperatures for specific ternary diagrams such as $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O}$, $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-CaO}$, and $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$, depending on coal type and the experimental atmosphere. It is possible, however, that the action of a fluxing agent may be enhanced in the presence of others and this may lead to the formation of a liquid phase at lower temperatures than those obtained from the three component phase diagrams.

Chapter 3

STUDIES OF SLAG DEPOSIT INITIATION USING A STICKING TEST

3.1 Introduction

Entrained slagging gasifiers are prime candidates for use in advanced Coal Gasification Combined Cycle power plants. They operate at temperatures well above the fusion temperature of the ash in the coal and produce no troublesome organic liquid by-products, such as phenols and tars. Reaction rates in slagging gasifiers are high, therefore, the equipment needed to gasify large quantities of coal is relatively small. However, the sensible heat of the gas produced is a relatively large portion of the total chemical energy available in the coal (12-15%). To increase the overall process efficiency, this sensible heat must be recovered prior to gas cleanup, which occurs at low temperature. Steam generation is the customary way to recover the sensible heat of the raw syngas. Thus, the gas is cooled down in a series of heat exchangers from about 1100-1300^oC to about 200^oC prior to quenching. The heat exchanger surfaces are cooled by high pressure water or steam. This limits the metal temperature of the heat exchanger surfaces to 250-700^oC, depending on the location in the heat exchange train, i.e., the economizer section, the evaporator section, or the superheater and reheater sections. During the cooling process, molten viscous ash particles can deposit on the heat exchanger surfaces. This will reduce the heat exchanger efficiency and may lead to serious corrosion and premature failure of the system.

There has been a considerable amount of work performed to explain the deposition of ash and subsequent fouling of heat exchanger

surfaces in pulverized coal boilers used in conventional power plants. A significant amount of practical experience has contributed to the development of methods to avoid excessive ash deposition and fouling in pulverized coal fired boilers. This experience is presently lacking for entrained slagging gasifiers. Thus, a basis for comparison of deposition and fouling in entrained slagging gasifiers and conventional boilers is urgently needed.

It was thus proposed to study the adhesion behavior of three coal ashes on four heat exchanger materials using the sticking test under both an oxidizing and a typical medium BTU gas (14.5 volume% CO_2 , 32.4 % CO , 25 % H_2 , 1 % H_2S , 27 % H_2O) (Abbott, 1984).

Preliminary results from this investigation have been reported by Abbott (Abbott, 1984). As an extension of this work, some of the tests were repeated to provide samples for mounting followed by vertical cross-sectioning. This exposes the interface between the slag drop adhered to the substrate so that it could be examined. In addition, it was postulated from the previous work that it was necessary for the surface to have an oxide layer in order for adherence to occur. However, it was never conclusively shown that the bonding of the drop to the surface was chemical in nature since an alternative mechanism 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 drop into these pores causes a mechanical anchoring after freezing. To test this alternative mechanism, an investigation of slag adherence on a reduced steel surface with high microporosity was conducted in this study under a reducing atmosphere (45 volume % CO , 25 % CO_2 , and 35 % H_2).

The four heat exchanger surfaces supplied by the Electric Power Research Institute (EPRI) included (1) T-11 steel (a 1 1/4 Cr, 0.5 Mo low alloy steel); (2) alonized T-11 steel (the above steel coated with aluminium using the pack aluminizing process); (3) flame-sprayed T-11 steel; and (4) SS 304 steel (stainless steel). The three high-rank bituminous coals used were Pittsburgh #8 (a hvb from Champion Plant, CONSOL, Pittsburgh); Illinois #6 (a hvb from River King Mine, Ill.); and Upper Hiawatha #1 (a hvb from Southern Utah Fuel Co., Coastal States). The minerals and mineral mixtures ($-38\text{ }\mu\text{m}$) examined included (1) pure pyrite; (2) 75% pyrite and 25% kaolinite; and (3) 12% pyrite, 2% Na_2O , 4% K_2O , 26% Al_2O_3 , 44% SiO_2 , 5% Fe_2O_3 , 2% C (to simulate a gasifier slag on heat exchanger surfaces). An ISI DS-130 scanning electron microscope with an energy dispersive spectrometer (a Kevex x-ray detector) (SEM-EDS) was used for the characterization at the interface morphology and chemistries of the ash drop adhered on the steel-based substrate. All photographically reproduced scanning electron microscopic images were recorded at 40 KeV on the DS-130. The automated SEM-EDS point-to-point analysis (stepwise $2\text{ }\mu\text{m}$ intervals) was conducted on a JEOL 50A SEM and a EDS interfaced to a Digital PDP 11/20 computer. The automated SEM-EDS can identify and measure the relative x-ray intensity of seven elements in each point and type the output data of the point according to the type of element and relative composition in that point.

3.2 The Sticking Test: Experimental Approach

3.2.1 Technique and Previous Use

The test was developed by Moza, Shoji, and Austin specifically

to study those factors which influence the adhesion or non-adhesion of a drop of molten ash to a metallic substrate (Moza, Shoji, and Austin, 1980). The test consists of forming a small pellet of powdered material (2 mm diameter by 2 mm high, weighing about 0.1 g) around a small hook in the end of a platinum wire (0.2 mm diameter). The pellet is heated in the center of the three nozzle ring burner system shown in Figures 3.1(a) and 3.1(b). The flame is a $\text{CH}_4\text{-O}_2$ flame whose flame temperature can be varied by changing the relative flow rates of CH_4 and O_2 , as measured by rotameters. As the powder pellet is heated, it fuses, melts and when the viscosity is low enough, a molten droplet falls off the wire. The droplet falls about 5 cm through the hole in a cap to a test substrate. The cap shields the substrate from radiation from the flame, and enables the temperature of the substrate to be accurately controlled by an auxiliary electric furnace plus a small platinum heater, also shown in Figure 3.1(a). The drop freezes on the substrate, the apparent contact angle is measured by an optical viewing system, and the drop is sheared off the hot substrate by a ram connected to a force measurement system, as shown in Figure 3.2. The test is repeated with identical pellets at increasing steps of substrate temperature.

Figure 3.3 shows the gas train for providing a simulated gasifier environment over the test substrate (14.5 volume% CO_2 , 32.4% CO , 25% H_2 , 1% H_2S , and 27% H_2O). The gas train consists of gas mixture supplier and a steam generator. The reducing gas mixture (CO , CO_2 , and H_2) and H_2S are premixed before it enters a preheated pyrex glass chamber. The glass chamber is heated and maintained at 250°C by an electrical resistance furnace controlled by a 120 volt, 7.5 ampere

TOP VIEW OF RING BURNER

SIDE VIEW OF STICKING APPARATUS

Figure 3.1(a). The sticking apparatus: diagram.

Figure 3.1(b). The sticking apparatus: photograph.

Figure 3.2. Device for measuring adhesion force.

Figure 3.3. Gas train for producing simulated gasifier gas at substrate temperature.

variable power supply. The steam is generated by heating water contained in a pyrex glass container in another electrical resistance furnace. The steam flow rate is maintained constant by the variac setting which is predetermined by calibrating the collected condensate rate with the variac reading. The water level in the container is kept constant by a constant head tank. The steam produced enters the preheated chamber and mixes with the premixed gases before it passes to the sticking furnace.

The technique was previously tested on four coal ashes (prepared by the high temperature ASTM ashing procedure), using a CH_4 - O_2 flame with an adiabatic flame temperature of 1750°C , and a pre-oxidized mild steel substrate (Moza and Austin, 1979, Abbott and Austin, 1982). It was found that the drop would not adhere when the substrate temperature was below a critical temperature, which is called the sticking temperature, typically 425 - 500°C , which is similar to the temperature of boiler wall tubes. Above this temperature, the adhesion strength increased roughly logarithmically with increase of substrate temperature. Although the behavior of the mean ash may not be a sufficient guide to slag deposits, the previous work showed that a roughly quantitative method for study of adhesion has been developed (Austin et al., 1983).

3.2.2 Experimental Procedure

The sticking test procedure used in this investigation involved the following sequence: making of the ash pellet, pretreatment of the substrate, melting of the ash pellet, and measurement of the adhesion force between the ash drop and the substrate. The pellet is formed

from low temperature pulverized coal ash (LTA ash) prepared by using the low temperature ashing method (Gluskoter, 1965), or from pure minerals, and mineral mixtures (ground to $-38\text{ }\mu\text{m}$). Ash or mineral pellets are made in a steel mold (4 mm diameter holes drilled in a steel plate 4 mm thick). A paste is formed by mixing about 5 grams of the ash or minerals with a drop of distilled water and two drops of ten percent polyvinyl alcohol solution. The steel mold is sprayed with a releasing agent (MS-122 supplied by Miller-Stephenson Chemical Co., Inc., Dannbery, Connecticut) and the 20 holes in the mold filled with the paste. A 20-30 mm length of 0.3 mm diameter platinum wire is inserted about half way into each pellet and the filled mold dried in an oven at about 110°C for one hour. After cooling, the pellets are carefully removed from the mold.

The substrate is a rectangular steel piece 35 mm by 19 mm by 6 mm. A hole for a platinum-10% platinum-rhodium thermocouple is drilled into the end of substrate closed to the upper surface. To make the thermocouple stay in place it is cast in alumina cement. The pretreatment conditions for substrates was as follows: the substrates were first wet polished with 240, 360, 400, and 600 grit silicon carbide paper. For tests under oxidizing conditions, the substrates were oxidized under the usual test conditions at 400°C for 20 hours in air. However, unlike the usual procedure, the surface treated substrates such as alonized T-11 and flame-sprayed aluminium coated T-11, were not polished before oxidation, to avoid the possibility of destroying the surface film. For tests under reducing conditions, the substrates were received from EPRI in a pre-sulfided condition; conditioning was for 140 hours at 300°C for T-11 and 150 hours at 500°C

for the other three substrates, in a typical medium BTU gas composition (14.5 volume% CO_2 , 32.5 % CO , 25 % H_2 , 1 % H_2S and 27 % H_2O). Since the pre-sulfided surface showed a weakly adherent layer that would easily break off during handling, substrates were also conditioned in the PSU laboratory by placing a polished T-11 steel in the holder of the sticking apparatus and conditioning in the medium BTU gas for 24 hours at 400°C . Figure 3.4 shows the SEM photomicrograph of T-11 steel sulfided in this manner (PSU-sulfided surface). The surface layer of sulfide was again brittle but much more adherent and not so easily broken off.

The investigation of the slag adhesion on a reduced steel surface required a special pretreatment of the substrate: a polished T-11 steel substrate (using the usual procedure) was oxidized in a furnace at 400°C in air for 20 hours. This substrate was then placed in the holder of the sticking apparatus and reduced with a flow of the reducing gas mixture (35 volume % H_2 , 45 % CO , and 20 % CO_2) at 500°C for 72 hours.

The flame used to melt the pellet was a fuel-rich flame with the CH_4 and O_2 flow rates at 970 and 850 ml/min respectively to give a flame temperature of $\sim 1600^\circ\text{C}$ as 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 a controlled temperature. Then 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 a stainless steel ram mounted on a top loading balance (Metler E2000) into contact with the

(a)

(b)

Figure 3.4. SEM photomicrographs of PSU-sulfided T-11 steel.
Magnification of (b) three times that of (a).

drop and raising the ram until shear occurred.

The procedure for mounting followed by vertical cross-sectioning of a sample of ash drop adhered on a substrate surface was as follows: the molten slag was dropped and adhered at a high substrate temperature (500°C) to give sufficient adherent strength for handling, and the substrate and drop were slowly cooled to room temperature. An epoxy resin (APCO 5315 part A) plus hardener (APCO 5315 part B), supplied by Applied plastic Co., Inc., (Now Hexel Co.,) El Segundo, California, was poured around the drop and substrate and allowed to set. The drop and substrate were cut vertically using an Isomet 11-1180 low speed saw (Beuhler Ltd., Evanston, Illinois). The cut face was polished in sequence on a polishing wheel with 240, 360, 400, and 600 grit silicon carbide paper and 0.3, 0.05 μm alumina powder with water. At the end of each polishing steps, the specimen was cleaned for 2 minutes in an ultrasonic bath (Cole-Parmer Instrument Co., Chicago, Ill.) to remove polished particles from the surface of specimen.

3.3 Results and Discussion

3.3.1 Adhesion Behavior for Slag Drops from Three Bituminous Coal Ashes on Four Steel Based Materials

The proximate and ultimate analyses, the spectrochemical analyses of high temperature ASTM ash (HTA), the mineralogical analysis of low temperature ash (LTA), and the ash fusion temperatures of HTA ash are given for the three tested coals in Tables 3.1, 3.2, 3.3, and 3.4, respectively. The sticking test results from the present work are compared to those of the previous results in Figures

Table 3.1. 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 3.2. 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 3.3. 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 3.4. 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).

3.5, 3.6, and 3.7. They were generally similar: the coal ash generally adhered more strongly to oxidized metal surfaces than to those with sulfided metal surfaces. The wide variability of Figures 3.5 and 3.7 was due to the poor adherence of the sulfided film of the supplied samples after shipping.

Figure 3.8 shows SEM photomicrographs of the interface between an Illinois #6 LTA drop adhered to the oxidized T-11 steel substrate in air. It can be seen that the drop wetted the oxide layer on the steel giving a smooth interface between the drop and steel. However, cooling to room temperature cracked the oxide layer from the steel. The drop cracked at the interface, showing the high thermal stresses produced on cooling to room temperature. Figure 3.9 illustrates the results of an automated SEM-EDS point-to-point (stepwise 2 μm intervals) analysis across the interface, indicating the gradual change in composition across the interface, from that of the drop to that of the oxide. Figure 3.10(a) shows the interface between the oxide layer of the T-11 steel and the drop; Figure 3.10(b) shows an iron map, with a low density of iron (plus holes) in the drop; Figure 3.10(c) shows a sulfur map, with no sulfur penetrating to the steel.

The SEM photomicrographs reveals the interface between an Illinois #6 LTA drop adhered to PSU sulfided T-11 steel under the reducing atmosphere, as shown in Figure 3.11. It is clear that there is no strong fusion of the drop to the sulfide layer; consequently, cooling produces no strong thermal stress and no cracking of the sulfide layer or the drop. Figure 3.12 gives the automated SEM-EDS point-to-point analysis across the interface, which tends to give erratic results due to the cavities in the path of the analysis.

Figure 3.5. Results of sticking test on presulfided T-11 steel under reducing conditions.

□ △ ◇ : substrate supplied by EPRI
 ■ ▲ : PSU-sulfided substrate.

Figure 3.6 Results of sticking test on alonized T-11 steel, oxidizing conditions.

□ △ ◇ : results from Abbott (Abbott, 1984).
 ■ ▲ : results from the present study.

Figure 3.7. Results of sticking test on sulfided alonized T-11 steel, reducing conditions.

□ △ ◇ : substrate supplied by EPRI
 ■ ▲ : PSU-sulfided substrate.

(a)

(b)

Figure 3.8. 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).

Figure 3.9. 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.

Figure 3.10. 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 3.11. SEM photomicrographs showing cross-section characteristic of interface between Illinois #6 LTA drop and sulfided T-11 steel substrate. Magnification of (b) ten times that of (a).

Figure 3.12. X-ray profiles of various elements as a function of distance from the interface, sulfided T-11 steel substrate(at left) and Illinois #6 LTA drop (at right).

The SEM photomicrographs of interface between an Illinois #6 LTA drop adhered to oxidized stainless steel in air is illustrated in Figure 3.13. The appearance is similar to 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. Figure 3.14 shows the results of Illinois #6 LTA drop adhered to PSU sulfided stainless steel under the reducing condition. There was a thin sulfide layer on the stainless steel, but the drop did not fuse into the layer and was not compatible with it.

Figures 3.15 and 3.16 show results of Illinois #6 LTA drop adhered to flame sprayed aluminum coated T-11 steel in air and the reducing condition, respectively. In both cases there is a definite Al layer on the substrate, with clear evidence of softening of this layer under the drop, but no strong fusion of the drop to the layer (see Figure 3.15). There is no evidence for the formation of a sulfide layer under the reducing condition.

Figure 3.17 is SEM photomicrographs showing the interface between Illinois #6 LTA drop adhered to alonized T-11 under oxidizing condition. There is no apparent oxide film on the surface and no strong fusion of the drop to the alonized layer. An automated SEM-EDS point-to-point analysis for Fe and Al at 50 μm intervals down from the alonized surface gave Al/Fe intensity ratios of 0.57, 0.40, 0.21, 0.16, and 0.10: this indicates penetration of Al even at 300 μm below the surface. Figure 3.18 illustrates the result of an Illinois #6 LTA drop adhered to PSU-sulfide alonized T-11. The appearance is similar to that under oxidizing condition, showing the resistance to sulfur attack on the surface and weak adhesion to the surface. An

Figure 3.13. 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 3.14. SEM photomicrographs showing cross-section characteristic of interface between Illinois #6 LTA drop and sulfided 304 SS stainless steel substrate. Magnification of (b) seven times that of (a).

Figure 3.15. SEM photomicrographs showing cross-section characteristic of interface between Illinois #6 LTA drop and oxidized flame-spray aluminium coated T-11 steel substrate. Magnification of (b) six times that of (a).

Figure 3.16. SEM photomicrographs showing cross-section characteristic of interface between Illinois #6 LTA drop and sulfided flame-spray aluminium coated T-11 steel substrate. Magnification of (b) three times that of (a).

(a)

(b)

Figure 3.17. SEM photomicrographs showing cross-section characteristic of interface between Illinois #6 LTA drop and oxidized alonized T-11 steel substrate. Magnification of (b) ten times that of (a).

Figure 3.18. SEM photomicrographs showing cross-section characteristic of interface between Illinois #6 LTA drop and sulfided alonized T-11 steel substrate. Magnification of (b) five times that of (a).

automated SEM-EDS point-to-point analysis showed no significant sulfur in the alonized layer, and the Al/Fe ratio varied in the same way as discussed above for the oxidizing condition. The surface of the steel, not the molten drop, cracked on cooling, but this appears to be due to stresses caused by differential contraction of the alonized layer rather than due to strong adhesion of the drop.

3.3.2 Adhesion Behavior for Slag Drops from Minerals and Mineral Mixtures on Four Steel-Based Materials

Tests were performed using a mineral mixture that simulated the composition of a gasifier slag collected from the heat exchanger surface in the gasifier (12 wt.% FeS, 2% Na₂O, 4% K₂O, 26% Al₂O₃, 44% SiO₂, 5% Fe₂O₃, 5% CaO, and 2% C). This was made by grinding the materials to pass through 400 mesh (~38 μm). The appropriate weights of Na₂CO₃, K₂CO₃, Fe₂O₃ and graphite (A.R. reagent grade, supplied from J.T.Baker Chemical Co., Phillipsburgh, New Jersey) were used to give the desired composition on melting in the reducing flame of the sticking test. This composition was tested on the PSU-sulfided T-11 steel: there was no sticking of drops from this composition at any substrate temperature. However, the result from the previous work showed that the gasifier slag actually did adhere on the tested substrate (Abott, 1984). The difference in adhesion behavior is possibly related to the difference in the form of chemical compositions contained in the mineral mixture and that of the gasifier slag. A higher temperature and longer time is required for the mineral mixture to produce sufficient amount of low melting point glass in order for the drop to adhere on the substrate. The gasifier

slag, on the other hand, already contains the low melting point glass necessary for adhesion on the substrate.

Previous experience has shown that pyrite and 75 wt% pyrite plus 25% clay mixtures gave strong adherence under oxidizing condition (Abbott and Austin, 1982). Figure 3.19 contains the SEM photomicrographs showing the interface of a drop of 75% pyrite plus 25% kaolinite mixture on oxidized T-11 steel at a temperature of 500°C. The drop wetted the oxide layer on the steel giving a smooth interface between the drop and steel, as noted in the SEM photomicrographs. A fracture was produced between the oxide layer and the steel when cooled to room temperature. The drop also cracked at the interface, showing the high thermal stresses produced on cooling. However, the SEM-EDS analysis of the drop section revealed that the drop was very heterogeneous, since a layer containing only Fe and S, probably iron sulfides, existed at the bottom of the drop. It is clear that some of the pyrite composition decomposes, melts, and flows to the bottom of the melting drop. When the drop falls onto the substrate, it is this layer which reacts with the oxide surface, not the mixture.

The mixture of pyrite and kaolinite of the same composition as above was also tested on the flame sprayed aluminium coated T-11 steel under oxidizing condition, giving the result shown in Figure 3.20. The iron sulfide layer was clearly compatible with the Al layer, and gave a strong bond. Figure 3.21 shows the results on alonized T-11 steel under oxidizing conditions at 500°C. Again, there was compatibility between the iron sulfide layer in the drop and the surface layer of substrate. Figure 3.22 shows the comparable result

Figure 3.19. 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).

Figure 3.20. SEM photomicrograph showing cross-section characteristic of interface between 75% pyrite plus 25% kaolinite drop and oxidized flame-sprayed aluminium coated T-11 steel substrate.

Figure 3.21. SEM photomicrographs showing cross-section characteristic of interface between 75% pyrite plus 25% kaolinite drop and oxidized alonized T-11 steel substrate. Magnification of (b) three times that of (a).

Figure 3.22. SEM photomicrographs showing cross-section characteristic of interface between pyrite drop and oxidized flame-sprayed aluminium coated T-11 steel substrate. Magnification of (b) three times that of (a).

for pyrite at a substrate temperature of 600⁰ C. Although the pyrite wetted the surface well, it required this high substrate temperature to give strong adhesion.

Since both types of mineral drops (pure pyrite, and the mixture of 75% pyrite plus 25% kaolinite) gave the same iron sulfide layer adhered to the oxide surface, it could be expected that both types of mineral drops would give the same adhesion strength. However, the results from previous work showed that the pyrite plus kaolinite drop gave much stronger adherence (10x) than the pure pyrite drop under oxidizing conditions (Abbott and Austin, 1982). It was noted from the present study that the time the pyrite pellet melted and fell off the platinum wire is much shorter (<0.5 minute) than that of the pyrite plus kaolinite pellet (>1 minute). This indicates that even at the flame temperature of 1600⁰ C, a pure pyrite drop would fall at a lower temperature because its viscosity and surface tension was lower than the pyrite plus kaolinite drop. As a consequence of lower temperature of the falling pyrite drop, the adhesion force was lower as compared to that of the pyrite plus kaolinite drop (Abbott, Conn, and Austin, 1985).

3.3.3 Adhesion Behavior for Slag Drops from Bituminous Coal Ashes and Mineral Mixtures on Reduced Steel Surfaces

The sticking behavior under the reducing condition (CO, CO₂, and H₂) was performed to evaluate the nature of adhesion of slag drop on the reduced T-11 surface. It was found that the 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 500⁰ C

on oxidized steel surface. Drops formed from the pyrite plus kaolinite mixture gave an adhesion force of 95 g at 500°C on the reduced steel surface, but the adhesion force was 1000 g at 500°C on oxidized steel surface.

Figure 3.23 compares SEM photomicrographs of the oxidized and reduced surfaces. Both surfaces are microporous (micrometer size range) but the reduced surface appears to have a higher porosity with larger pores. The adhesion of the drop formed from the pyrite plus kaolinite was sufficient to enable the drop and substrate to be encapsulated in resin. Figure 3.24 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 reports only Fe and S by SEM-EDS, plus glass containing Al, Si, and Fe in the center, plus some regions of mechanical mixture of the base components. It appears that 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 containing the interface is FeS. This 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 microporosity.

3.4 Summary

The results from the sticking test in this investigation can be summarized as follows:

- (1) Slag drops on an oxide layer on T-11 steel under oxidizing

(a)

(b)

Figure 3.23. SEM photomicrographs of (a) the oxidized steel surface; and (b) the reduced steel surface.

Figure 3.24. SEM photomicrographs of the polished cross-section of ash drop on (a) oxidized steel surface and (b) reduced steel surface.

conditions appeared to be compatible with the layer and tended to give strong adherence. The logarithmic increase of strength with increasing substrate temperature was the typical adherence behavior of slag drops on oxidized steel. Cross-sections of interfaces between slag drops and the oxidized surface of T-11 steel showed that there was a strong fusion of the drop to the oxide layer, which produced high thermal stresses and subsequent cracking in the drop upon cooling to room temperature.

(2) The oxide film on 304 SS stainless steel appeared to be much thinner, with a less spongy structure than that on T-11 steel. The sticking of slag drops on this substrate occurred at higher substrate temperature than for T-11 steel. Cross-section of the interface between slag drop and the oxidized surface of this material showed similar appearance to that of T-11 steel.

(3) The T-11 steel with sulfiding pretreatment showed a weakly adherent sulfided layer. Slag drops on this substrate under reducing condition appeared less compatible than on oxidized layers and there was no large increase in strength with increasing substrate temperature, although weak adherence did occur at relatively low temperatures ($\sim 200^{\circ}\text{C}$). This was due to adhesion to the surface sulfided layer and fracture via detachment of this layer. Cross-section of the interface between slag drop and the sulfided surface of T-11 steel exhibited no strong fusion of the drop to the sulfide layer; consequently, cooling produced no thermal stress and no cracking of the drop.

(4) The sulfided flame sprayed aluminum coating on T-11 steel was not significantly different in appearance from the oxidized

surface of this substrate, indicating resistance to attack by sulfur-containing gas. The coating prevented very strong sticking, but appeared to soften enough to give fairly weak adherence, under both oxidizing and reducing conditions. Cross-sectioning results of adherence of slag drops on this substrates in both environmental conditions exhibited a definite aluminium layer on the substrate with clear evidence of softening of this layer under the drop, but no strong fusion of the drop to the layer.

(5) The alonized T-11 steel surface appeared to resist oxidation or sulfidization. This is presumably due to the presence of alloy (Al/Fe) on the surface. Cross-section results for both oxidizing and reducing conditions exhibited no strong fusion of the drop to the alonized surface.

(6) It was concluded that the alonized T-11 surface was superior (in resisting the formation of strong slag initial layer) to 304 SS stainless steel which was superior to T-11 steel, especially under reducing conditions. The flame sprayed aluminium coated surface did not appear from the sticking test to be a feasible substrate, because of the softening of the top layer of this surface.

(7) The high adhesion strength of the molten ash drop to the oxide layer on oxidized steel is due to chemical compatibility between the oxide layer and the ash and not a result of mechanical anchoring in microporosity.

(8) A comparison of the dependence of composition of ash drops in the present investigation to sticking behavior is difficult because it was observed that the temperature of the tested drops prior to being dropped on the substrate might not be the same. Since the

adhesion is strongly affected by the temperature of the drop, this introduces an uncontrolled variable when comparing results from one ash or mineral to another.

Chapter 4

STUDIES OF BOILER SLAG DEPOSIT FORMATION USING
A VERTICAL EXTERNALLY-HEATED TUBE FURNACE4.1 Introduction

The investigation of slag deposit initiation using the sticking test suffers from several disadvantages. For instance, the drops are much larger (~3000 μm diameter) than the fly ash drops formed on pulverized coal combustion and the test conditions do not closely simulate the time-temperature history and the environment in the utility boiler. In the sticking test, the temperature of the drop when it releases from the platinum wire depends on viscosity and surface tension of the drop, and this introduces an uncontrolled variable when comparing results from one coal to another. From these reasons, a new test was devised to overcome the inherent limitations of the sticking test (Abbott, 1984). The new test used a vertical externally-heated tube furnace which burned pulverized coal passed in a thin stream down the tube heated to simulate the time-temperature history of a pulverized coal flame in the 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, and the initiating layer examined.

The vertical externally-heated tube furnace was utilized in the present study to investigate the mechanisms of ash deposit formation relevant to wall slag deposit in the utility boiler. A sufficient

growth of adherent deposit was essential for an examination to be made of the deposit from the initial ash layer at the oxidized steel surface to the last surface of the ash deposit. The previous procedure and conditions of the vertical externally-heated tube furnace was therefore adapted to grow a deposit that could be weighed, vertically cross sectioned, and examined in a variety of ways.

Nine coals of both high- and low-rank coals were studied: (1) Illinois #6, a high-volatile bituminous from River King Mine (Peabody), Ill.; (2) Pittsburgh #8, a high-volatile bituminous from Champion Plant (CONSOL), Pa.; (3) Upper Hiawatha #1, a high-volatile bituminous from Southern Utah Fuel Co., Coastal States (SUFCO), Utah; (4) Upper Freeport, a medium-volatile bituminous from Upper Freeport Seam, Pa.; (5) Tunnelton, a medium-volatile bituminous from the Marion Mine, Upper Freeport Seam, Pa.; (6) Decker, a subbituminous, Montana; (7) Powder River Basin, a subbituminous from the Powder River Basin, Wyoming; (8) Texas, a lignite from the Wilcox formation, Texas; (9) North Dakota, a lignite from the Beulah-Zap Seam, Nd.

In addition, synthetic coals prepared from known minerals dispersed in a polymer were also investigated to identify the inorganic constituents and compositions which are most prone to both adhere and sinter, resulting in significant slag build-up. The approach was to observe the high temperature transformation and reaction of synthetic coals containing individual mineral or binary mineral mixtures to assess their significance in the deposit formation process. The tested synthetic coals included: (1) polymer+pyrite; (2) polymer+illite; (3) polymer+quartz; (4) polymer+pyrite+illite; (5) polymer+pyrite+kaolinite; and (6) polymer+pyrite+quartz. A synthetic

coal having a mineral composition and amount to match the mineralogy of an Illinois #6 coal was also tested and compared to evaluate whether the synthetic coal would produce fly ash and form a deposit having similar characteristics to the actual coal.

4.2 Experimental Technique and Procedure

The general arrangement of the test system is shown in Figure 4.1(a), and Figures 4.1(b), 4.1(c), 4.1(d), and 4.1(e) show further details. The muffle furnace tube of 99.8% fused alumina (6.35 cm internal diameter by 90 cm long) has a maximum temperature zone of about 50 cm long. It is heated by three tangentially-fired natural gas-air burners and the temperature is controlled by adjusting the air-to-fuel ratio. In general, gas temperatures along the center line of the furnace tube are about 30°C lower than corresponding wall temperatures at the same position within the furnace hot zone.

The coal feed system consists of a fluidized-bed feeder which entrains pulverized coal of 250 μm x 45 μm in a primary air stream (~1 liter/min.). The feeder assembly rests on a balance to monitor continuously the coal feed rate. This mixture of coal and air is injected into the furnace through the water-cooled injector probe. Preheated secondary air (~3 liter/min.) enters the furnace through a flow straightener. Since the diameter of the injector tip is small (0.32 cm), the linear velocity of the gas there is higher (207 vs 2 cm./sec) than at the secondary annulus (diameter 3.81 cm). The gas velocity profiles at various axial positions at the hot zone temperature (1500°C) in the vertical externally-heated tube furnace were calculated using the method developed by Tsai (Tsai, 1985). This

Figure 4.1(a) Vertical externally-heated tube furnace system.

Figure 4.1(b). Vertical externally-heated tube furnace; injector and preheater section.

Figure 4.1(c). Vertical externally-heated tube furnace;
fluidized bed feeder.

Figure 4.1(d). Bottom of vertical externally-heated tube furnace; constrictor and test substrate.

Figure 4.1(e). Pipe/cyclone ash probe.

is a numerical computer solution of the Navier Stokes equations using appropriate boundary conditions at the entrance to the furnace tube and at the walls. The result is shown in Figure 4.2: 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 velocity profile (21.6 cm/sec) with the main stream. From this gas velocity profile, the gas velocity of 21.6 cm/sec at the center line was used to calculate the particle residence time within the hot zone (50 cm) to be 1 to 2 seconds, assuming a particle of 100 μm with a density of 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 (a 1.3 cm in diameter ceramic nozzle) prior to impingement on the substrate, which is held at a controlled temperature simulating a boiler steel heat transfer surface. Exit gases are removed by a vacuum pump to prevent back-pressure build-up in the furnace tube.

Modifications to the system reported previously (Abbott, 1984) included placing the collection probe on a movable platform so that it can be readily lowered for examination, and separating the mounting of the alumina sheath and constrictor from the probe. Thus the substrate can be lowered and viewed, leaving the alumina sheath and constrictor in place to avoid cracking of the sheath, which occurs if it is also suddenly lowered. Gaps between the collector probe, the alumina sheath and the bottom of the furnace were sealed with high temperature fiber packing to prevent back pressure and air inleakage. A sufficient seal was achieved by tightening the entire collector

Figure 4.2. Gas velocity profile in the vertical externally-heated tube furnace: L is the distance along the tube furnace.

probe system with the adjustable platform. In addition, the temperature measuring system on the collector probe which previously utilized a Pt/Pt-Rh system was replaced by an Inconnel-shield Cr/Al thermocouple, which was suitable for the substrate temperature of 200-600°C and was more robust.

In some tests fly ash was formed and collected without the deposition probe in place by attaching the sampler shown in Figure 4.1(e). A size fraction of coal of 60x325 mesh was prepared by sieving from the ground coal. The substrate was a cylinder steel piece 3.81 cm in diameter by 0.64 cm thickness. It was a mild carbon boiler steel supplied by Babcock and Wilcox Company, Ohio. A hole for an Inconnel-shield Cr/Al thermocouple was drilled from the edge into the center of the substrate closed to the upper surface. The substrate was polished sequentially with 240, 360, 400, and 600 grit silicon carbide paper with water on a polishing wheel and subsequently oxidized in a muffle furnace at 400°C in air for 20 hours, and its weight measured.

The procedure for ignition and heat-up of the vertical tube furnace has been well documented by Abbott (Abbott, 1984). The furnace was normally operated with a hot zone of 1500°C (wall temperature). The gas temperature passing through the annulus around the substrate was 1100°C and the temperature seen by the deposit was between 1300°C and 1100°C. These temperatures were obtained by the use of pyrometric cones (supplied by the Edward Orton Jr. Ceramic Foundation, Columbus, Ohio), 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 g/minute. The constrictor dimensions of 1.3 cm gave gas velocities within the range 3 to 4 m/s. In some tests, the gas velocities were reduced to approximately 0.6 m/s by using a constrictor dimension of about 3.2 cm in diameter. In other tests, the constrictor nozzle was designed with the hole cut at a 60° angle to the horizontal for reduction of direct radiation from the furnace onto the substrate. In the tests reported here the substrate in the collector probe was maintained at a temperature of $500 \pm 5^{\circ}\text{C}$ before starting deposition.

An ISI DS-130 scanning electron microscope equipped with an energy dispersive spectrometer (a Kevex x-ray detector) (SEM-EDS) was used for the characterization of the deposit morphology and chemistry. All photographically reproduced scanning electron microscopic images were recorded at 40 keV on the DS-130. A Phillips APD 3600 automated x-ray diffraction unit equipped with CuK_{α} source operated at 1200 kVA, condensating slits and diffracted beam graphite monochromator was used to generate the x-ray diffraction patterns. X-ray patterns were accumulated from 10 to 70° 2-theta at 0.5 seconds per 0.02° 2-theta to assure sufficient time to discriminate low intensity peaks from the background. The resulting patterns were analyzed by a computer program that assigns d-spacings to each peak using the 2-theta value and peak intensity. A search-match routine was then used to identify the compounds present by comparison with the JCPDS data base. The final selection of a species is based on a process of elimination and the chemical analysis.

In addition, examination was made of deposits vertically cross-sectioned through the deposit and substrate. Deposit and

substrate were mounted in an epoxy resin (APCO 5315, part A) plus hardener (APCO 5315 part B), supplied by Applied Plastic Company, Inc., (now Hexel Co.,) El Segundo, California. The deposit and substrate were cut vertically by a low speed diamond wafering blade (Isomet 11-1180 low speed saw, Beuhler Ltd., Evanston, Illinois). The cut surface was then polished in a sequence on a polishing wheel with 240, 360, 400, and 600 grit silicon carbide paper and 3, 1, 0.25 μ m diamond paste, in lapping oil. At the end of each polishing steps, the specimen was cleaned for 2 minutes in an ultrasonic bath to remove polished particles from the polished surface (Cole-Parmer Instrument Co., Chicago, Illinois).

The polymer which was used as an organic portion of the synthetic coal is a copolymer consisting of polyester, styrene and divinyl benzene. The following components are used in the preparation of the polymer:

(1) Polymer (polyester): The polymer is a linear polyester containing saturated and unsaturated aliphatic units. The unsaturated units provide sites for crosslinking. The relative proportions of the saturated and unsaturated units determines the degree of crosslinking: the higher the unsaturated units, the greater possibility of crosslinking.

Chemical formula:

(2) Monomer (styrene and divinyl benzene): The monomer contains a vinyl group on the benzene ring that can polymerized (cross-linked)

with the linear unsaturated polyester via a free radical reaction.

Chemical formula:

styrene

divinyl benzene

(3) Initiator (peroxide compound): The initiator, methyl ethyl ketone peroxide, is used for cold curing (room temperature) of the unsaturated polyester.

Chemical formula:

(4) Accelerator (tertiary amine): In the presence of the accelerator, dimethylaniline, the initiator rapidly decomposes without the application of heat into free radical.

Chemical formula:

dimethylaniline

The final cured copolymer is produced by a series of reaction steps which includes the aforementioned components:

Step 2:

Step 3:

The crosslinking results in the formation of covalent bonds consisting of one or more monomer units between the polyester chains. Cured copolymer products containing both styrene and divinyl benzene are more highly crosslinked, and therefore harder, more heat resistant and more brittle than those containing styrene alone because of the two vinyl groups on the benzene ring of divinyl benzene. Typical crosslinked structure of the cured copolymer (polyester-styrene-divinyl benzene) is as follows:

Mixtures of minerals and polymer to simulate a synthetic coal were prepared as follows. The polymer is a mixture of 75 volume percent resin (a polyester dissolved in styrene, supplied by the Fiber Glass Evercoat Co., Inc., Cincinnati, Ohio) and 25 volume percent divinyl benzene (DVB), supplied by the Polyscience Inc., Warrington, Pennsylvania, added for brittleness. The initiator is methyl ethyl ketone peroxide (MEKP) at a level of 7.3 ml per 1000 ml of resin/DVB, in the resin as purchased. The DVB as purchased contained an inhibitor to enhance its shelf life, and this was removed by extraction with an equal volume of 2N aqueous ammonium hydroxide (A.R. reagent grade, supplied by J.T.Baker Chemical Co., Phillipsburg, New Jersey) in a separating funnel. Any moisture remaining in the

de-inhibited DVB was removed with a few grams of anhydrous magnesium sulfate (A.R reagent grade, supplied by Fisher Scientific Co., New Jersey). If some flakes of magnesium sulfate remained it was assumed that enough was used; if it all clumped more was added. The magnesium sulfate was then removed by filtration. The desired volume of resin was measured and poured into a 2 liter Pyrex dish, and mixed with a stirring paddle. The cleaned DVB was then added slowly while stirring. The MEKP was added and a spatula used to scrape the bottom in addition to the use of stirrer, to ensure good mixing. The polymer set up within an hour to the point that mixing in minerals was impossible, but the initial mixture was not viscous enough to support pyrite. Therefore the minerals were added at the beginning and the stirring continued until the minerals no longer sank. The polymer was then allowed to finish reacting for about 12 hours, removed from the dish, and hardened by heating the block at 75 °C in an oven equipped with exhaust fan overnight. The material was then reduced in size in stages using a hammer, a jaw crusher, and a grinder. It was then ground to final pulverized coal size in a laboratory roll-race mill using alloy steel rolls and race. Ground minerals were also prepared in this mill and the minus 400 mesh (38 µm) material classified in a Donaldson air classifier to prepare minus 20 µm material for incorporation into the polymer.

4.3 Results and Discussion

4.3.1 Slag Deposit Formation from Several Coals

Table 4.1 gives the analysis of the coals tested which cover a range of coal rank. Upper Hiawatha #1 ranks as a bituminous high-rank

Table 4.1(a). 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	hvb	hvb	hvb	mvb	mvb	Sub.	Basin 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 4.1(b). 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 4.1(c). Spectrochemical analysis of high temperature ash (ASTM) of test coals.*

Coal	Powder								
	Illinois #6	Pittsburgh #8	U.Hiawatha #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 4.1(d). Fusion temperature of high temperature ash (ASTM) of test coals, °C.

Coal	Illinois #6	Pittsburgh #8	U.Hiawatha #1	U.Freeport	Tunnelton	Decker	Fowder 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 4.1(e). 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 4.1(f). 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.

coal but has the behavior of a low-rank coal as far as slagging is concerned. Examination of deposits collected on the probe or 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 Powder River Basin coal passed through the furnace in 30 minutes gave deposits masses of 313, 324, 302, and 311 μg , showing good reproducibility, and collection of about 65% of the high temperature ASTM ash.

Table 4.2 gives the deposit rates for the test coals under the same conditions. Figure 4.3 shows the variation of deposit mass with time. As expected, as the deposit grows, the rate of deposition increases since the top of the deposit will become hotter. Figures 4.4(a) and 4.4(b) show the deposition rates estimated by differentiation of the curves of Figure 4.3, normalized by dividing by the rate of firing of high temperature ASTM ash in the 0.33 g/minute of coal. These figures emphasize the differences in the way deposit grows: Illinois #6, for example, shows a strongly accelerated rate of growth whereas Tunnelton and the low-rank coals shows a much uniform rate of deposition. Most of the bituminous coals (except Tunnelton) reached a sticking coefficient close to 1 at the end of deposition time of 30 minutes, showing that when deposit reaches a certain height, the top of deposit can give virtually complete capture of the fly ash. However, at the longer deposition time (up to 90 minutes), the sticking coefficient decreases, probably because as the deposit grows toward the constrictor, the changing of deposit shape alters the flow of gas around the deposit. Consequently, there appears to be a

Table 4.2. 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

^aGas velocity through constrictor = 3.5 m/sec.

^bGas velocity through constrictor = 0.6 m/sec.

Figure 4.3. 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 4.4(a). 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 4.4(b). 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.

fraction of fly ash entering the nozzle that simply by-passes over the deposit. One remarkable result is the entirely different behavior of the two Upper Freeport coals (Upper Freeport coal and Tunnelton coal), which have almost identical ash compositions, yet give entirely different deposit behavior.

The gas-particle stream was accelerated as it passed through the constrictor and 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 physical appearance of a cone or mountain that grows in the direction of the incoming hot gases, as illustrated for the tested coals in Figure 4.5. It was quite easy to see the direction of gas flow indexed by the growth lines in the deposit. This provides the striking evidence that the mechanism of growth is direct head-on impingement, while particles skimming a surface may not stick to it.

Four different locations on a deposit were examined: (1) the thin layer of dust dispersed over the substrate around the deposit mass (dust material); (2) the base of the deposit mass (lower portion of deposit mass); (3) half-way up the mass (upper portion of deposit mass); and (4) the top portion of the deposit mass. Figure 4.6 shows SEM photomicrographs of these materials at the various portions of deposit. The general structure was: (1) dust material: fine spheres (mainly 2-5 μm) covered the substrate surface which could not be easily blown from the surface; (2) lower portion of

Figure 4.5(a). 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 4.5(b). Appearance of deposit for (a) Texas; (b) Decker; (c) North Dakota; and (d) Powder River Basin.

Figure 4.6(a). SEM photomicrographs of deposit from U. Freeport coal; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top of deposit mass.

Figure 4.6(b). SEM photomicrographs of deposit from U. Hiawatha #1 coal; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top of deposit mass.

Figure 4.6(c). SEM photomicrographs of deposit from N. Dakota lignite; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top of deposit mass.

deposit mass: the spheres (mainly 10-15 μm) appeared to be loosely sintered together, with substantial porosity. The color was somewhat darker, especially on the outside of the deposit; (3) upper portion of deposit mass: the spheres (mainly 25-50 μm) were definitely fused together with lower porosity; and (4) top portion of deposit mass: the material appeared to be almost completely fused with evidence of crystallization from a melt.

Obviously, as the deposit grows the top of the deposit grows into the regions of higher temperatures closer to the constrictor, leading to sintering and melting of the deposit particles. The average size of deposited ash particles was large compared to the dust material, indicating that the ash particles adhered and form a deposit probably mainly by inertial impaction, whereas the smaller dust particles tended to follow a streamline of flue gas and deposited by a particle-diffusion process (Brownian and/or thermophoresis). The mass could be easily broken at a layer near the substrate, and loose ash brushed off, leaving a layer of particles strongly adhered to the oxide film on the substrate.

These adherent materials of deposits from high- and low-rank coals are compared in Figure 4.7, showing that the adherent materials from low-rank coals are less deformed than those of the high-rank coals. The strongly adherent material appeared to be bonded to the oxide film on the substrate and could be removed only by scraping with a sharp metal edge, also breaking away the oxide film, which was left adhering to the particles. There was slight sintering between particles. The adherent particles were larger (mainly 35-50 μm)

Figure 4.7(a). SEM photomicrographs of adherent material from (a) Illinois #6; (b) U.Freeport; (c) Pittsburgh#8; and (d) Tunnelton. Note that these particles are flattened and deformed as compared to those of the low-rank coals (see next Figure).

Figure 4.7(b). SEM photomicrographs of adherent material from (a) N.Dakota; (b) Powder River Basin; (c) Texas; and (d) Decker.

compared to most fly ash particles, indicating that they probably adhered to the substrate by inertial impaction.

The general structure of the deposits is compared in Table 4.3: lower portion of deposit mass always gave a weak, slightly sintered structure. A qualitative SEM-EDS analysis of the deposits gave the results in Table 4.4. The results of spectrochemical analysis performed on selected regions of the deposits are summarized in Table 4.5. The concentration of Fe_2O_3 for most of the high-rank tested coals (except Upper Hiawatha #1) generally showed higher Fe_2O_3 content in the deposit as compared to that in the high temperature ASTM ash analysis. This trend was not found in the low-rank tested coals (except Decker). The changes exhibited by SiO_2 were relatively small and the concentration appeared to remain essentially constant irrespective of the position in the deposit from high-rank coals: Upper Hiawatha #1 is an exception, however.

The deposits from low-rank coals, on the other hand, exhibited higher SiO_2 concentration as compared to their high temperature ASTM ash compositions (except Powder River Basin coal). The SiO_2 concentration trend was found to correspond with that of CaO , suggesting that CaO probably reacts with quartz, and clays to form calcium complex silicates causing them to be sticky and thus more prone to deposit: Decker is an exception, however.

The changes exhibited by Al_2O_3 were relatively small and the concentration appeared to remain essentially constant irrespective of the position in the deposit, the type of coals, or compared to the high temperature ASTM ash. This may indicate that most of the clays constantly participate in the ash deposit build-up for most of the

Table 4.3. 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 4.4. Peaks of SEM-EDS spectra on deposits.

Coal	Dust material	Lower and upper portion of deposit mass	Top of deposit mass
<u>High-rank</u>			
U.Freeport Tunnelton Pittsburgh #8	Al,Si,K,Ca,Fe,Ti, but no Na and S.	Si,Fe higher, Ca,Ti, lower than dust material; no Na and S.	High Si, lower Al,K,Fe, traces Ca, Ti; no Na and S.
Illinois #6			
	Al,Si,K,Ca,Fe,Ti, Na, and S.	Same as above; now no Na and S.	Same as above.
<u>Low-rank</u>			
U.Hiawatha #1* Powder River- Basin Decker	Al,Si,K,Ca,Fe,Ti, Na, and S.	Same as dust material; but higher Ca; lower Na and S.	High Si; lower Al,K,Ca,Fe, traces Mg,Ti, no Na and S.
N.Dakota			
	Same as above, but Na and S highest.	Same as above.	Same as above.
Texas	Same as above, but Na, and S lowest.	Same as above, but no Na and S.	Same as above.

* U.Hiawatha #1 is a high-rank coal but has the behavior of a low-rank coal.

Table 4.5(a). 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 4.5(b). 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 4.5(c). 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 4.5(d). 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 4.5(e). 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 4.5(f). 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 4.5(g). 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 4.5(h). 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 4.5(1). 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.

tested coals. The high temperature ASTM ashes exhibited higher Na_2O concentration (except Texas lignite) as compared to those of their deposits, indicating that a portion of sodium retains in the high temperature ASTM ash but most of sodium vaporizes in the coal flame under the present conditions. However, significant amount of sodium and sulfur species were found concentrated in the dust material around the edge of the substrate and along the cooled collecting probe near the furnace exit, indicating that most of the sodium and sulfur follow the flue gas stream and some fractions had condensed on the cooled region.

X-ray diffraction analysis was performed for material from various regions in the deposits. The results are given in Tables 4.6 and 4.7. Comparison with the analysis of the fly ash, using Illinois #6 as an example, shows that a number of crystalline phases occur, especially at the top of the deposit, which are not present in the fly ash. This is to be expected as the top of the deposit became sufficiently melted allowing interactions between the deposited components. The formation of alkali-aluminosilicates (such as anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$) as predicted by the phase diagram are likely to occur at some locations in the melt.

Of more interest is the variation of composition occurring in the initial stages of the deposit. Cross-sectioning of the deposit allowed more detailed investigation of the structure and chemistry of the deposit. Figure 4.8 shows a typical cross-sectioned deposit from a low-rank coal, using the Powder River Basin coal as an example. The deposit shows three clear regions: (1) a dust material; (2) a dense

Table 4.6(a). X-ray diffraction analyses from regions at various locations in deposits and fly ash from high-rank coals: Upper Freeport and Tunnelton coals.

Coal	Location	Phase present		
		Major	Minor	Trace
U. Freeport	1 (dust material)	Quartz, SiO_2 Mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	Hematite, Fe_2O_3 Glass Magnetite, Fe_3O_4	Fassaite, $\text{Ca}(\text{Mg}, \text{Fe}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$
	2/3 (lower portion of deposit mass)	Mullite Hematite Glass	Magnetite Quartz Spinel, MgFeAlO_4	
	3/4 (top portion of deposit mass)	Glass Mullite Hematite	Magnetite Spinel	Fassaite
	Fly ash	Glass Mullite Hematite		
Tunnelton	3/4 (top portion of deposit mass)	Mullite Quartz Glass	Hematite	Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ Gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ Hercynite, FeAl_2O_4

Table 4.6(b). X-ray diffraction analysis from regions at various locations in deposit and fly ash from high-rank coal: Illinois #6 coal.

Coal	Location	Phase present		
		Major	Minor	Trace
Illinois #6	1 (dust material)	Quartz Hematite Glass	CaSO_4 Mullite	Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ Augite, $\text{Ca}(\text{Fe}, \text{Mg})\text{Si}_2\text{O}_6$ Lime, CaO $\text{Na}_2\text{Ca}(\text{SO}_4)_2$
	2/3 (lower portion of deposit mass)	Glass Quartz Hematite Magnetite Lime	Mullite CaSO_4	
	3/4 (top portion of deposit mass)	Quartz Hematite Glass	Anorthite Augite Corundum, Al_2O_3 Spinel Mullite	
	Fly ash	Quartz Hematite CaSO_4 Glass	Mullite	

Table 4.6(c). X-ray diffraction analyses from regions at various locations in deposit and fly ash from high-rank coal: Upper Hiawatha #1 coal.

Coal	Location	Phase present		
		Major	Minor	Trace
U.Hiawatha #1	1 (dust material)	Quartz Glass	Anorthite Corundum CaSO ₄ Hematite Metakaolinite, Al ₂ SiO ₅	(Na _{0.8} Ca _{0.1}) ₂ SO ₄
	2/3 (lower portion of deposit mass)	Quartz Anorthite	Gehlenite, Ca ₂ Al ₂ SiO ₇ Mullite	Hematite
	3/4 (top portion of deposit mass)	Quartz Glass	Hematite	Anorthite
	3/4 (60° angled constrictor) (top portion of deposit mass)	Quartz Glass	Anorthite	CaSO ₄ (Na _{0.8} Ca _{0.1}) ₂ SO ₄ Hematite Akermanite, Ca ₂ MgSiO ₇
	Fly ash	Quartz CaSO ₄ Glass	Gehlenite Lime	Hauyne, (Na,Ca) ₄₋₈ (AlSiO ₄)(SO ₄) ₁₋₂ Spinel, Mg(Al,Fe) ₂ O ₄

Table 4.7(a). X-ray diffraction analyses from regions at various locations in deposits from low-rank coals : Powder River Basin and Decker coals.

Coal	location	Phase present		
		Major	Minor	Trace
Powder River Basin	1 (dust material)	Gehlenite Quartz (Fe,Mg,Ca)SiO ₃ Lime Glass	Akermanite Hematite Periclase,MgO (Na _{0.8} Ca _{0.1}) ₂ SO ₄	CaSO ₄
	2/3 (lower portion of deposit mass)	Gehlenite Fassaite (Fe,Mg,Ca)SiO ₃ Augite	Anorthite Akermanite Glass	Albite,NaAlSi ₃ O ₈
	3/4 (top portion of deposit mass)	As for 2/3 but better crystallization of phases.		
Decker	3/4 (60° angled constrictor) (top portion of deposit mass)	Gehlenite (Fe,Mg,Ca)SiO ₃ Quartz	Anorthite Augite Akermanite	CaSO ₄
	3/4 (top portion of deposit mass)	Quartz Glass Mullite Anorthite	Gehlenite	Hematite

Table 4.7(b) X-ray diffraction analyses from regions at various locations in deposits from low-rank coals; North Dakota and Texas lignite coals.

Coal	Location	Phase present		
		Major	Minor	Trace
N.Dakota	1 (dust material)	Na_2SO_4 Glass	CaSO_4 Hematite Nephelene, NaAlSiO_4	Quartz
	2/3 (lower portion of deposit mass)	Gehlenite Hematite Akermanite	CaSO_4 $(\text{Na}_{0.8}\text{Ca}_{0.1})_2\text{SO}_4$ Lime	
	3/4 (top portion of deposit mass)	As for 2/3 but better crystallization of the major phases and less crystallization of the minor phases.		
Texas	1 (dust material)	Glass Quartz	CaSO_4 Hematite	$(\text{Na}_{0.8}\text{Ca}_{0.1})_2\text{SO}_4$
	3/4 (top portion of deposit mass)	Glass Quartz Anorthite Albite, $(\text{Na}, \text{Ca}(\text{AlSi})_4\text{O}_8$	$\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}$

Figure 4.8. SEM photomicrographs of cross-sectioned deposit from Powder River Basin coal: (a) dust material; (b) a layer of loosely sintered spheres; (c) a higher layer of stronger sintering with growth lines in the direction of gas flows; and (d) a strongly sintered and fused top (black areas are the impregnating resin).

layer of particles at the center of deposit mass; (3) a succeeding layer of higher porosity, with growth lines in the direction of the flow, and the appearance in the mass of darker particles; and (4) the higher in the deposit the more fused the particles. Also the longer deposition time, the more fused at the top of deposit mass, as shown in Figure 4.9. A typical cross-sectioned deposit from a high-rank coal, Pittsburgh #8, having high glassy phase, crystals embedded in the glassy phase and pores of various sizes, is shown in Figure 4.10. Due to the flow patterns established by the constrictor over the substrate surface, the average particle size of the deposited particles decreased from the center to the outer edges of the deposit, see Figures 4.11(a) and 4.11(b) as an example.

Figure 4.12 gives clear evidence of hemispherical particles spread on the oxide layer, forming an initiating layer for the Powder River Basin deposit. These flattened particles were analyzed by SEM-EDS, and 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 higher locations in the deposit mass gave major peaks of Ca, Al, Si, and Fe, but neither Na nor S were seen at higher regions in the deposit. 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. The EDS spectrum showed that this type of particle contained mostly Fe with traces of Al and Si.

Type 2: glassy black spheres with smooth surface texture were

Figure 4.9. SEM photomicrograph of cross-sectioned deposit for N. Dakota lignite (coal feeding time = 90 min.). Note that the top portion of deposit mass fused with less porosity as compared to that of the lower portion of deposit mass. (Black areas are the impregnating resin).

Figure 4.10. SEM photomicrographs of cross-sectioned deposit from Pittsburgh #8 coal at various magnifications (upper portion of deposit mass), showing high glassy phase, crystals embedded in the glassy phase, and various sizes of pores in the deposit mass.

Figure 4.11. SEM photomicrographs of cross-sectioned deposit from U.Hiawatha #1 coal: (a) at the edge of substrate; (b) at the edge of deposit; (c) at the center of deposit; and (d) same as (c) but at higher magnification; note that the deposited particle sizes are different between (a) and (b), black areas are the impregnating resin.

Figure 4.12 Strongly adherent particles forming an initiating deposit layer: deposit from Powder River Basin coal.

also found. The EDS spectrum showed that 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. The EDS spectrum showed that this type of particle gave a large peak for Ca as well as a large peak for Fe, with smaller peaks of Al and Si.

Type 4: black particles with a smooth surface texture containing Al and Si with a trace of Fe.

Type 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 Pittsburgh #8 along with the other types. The black particles of type 1 were often deformed and flattened against the oxide film, showing that the particles were molten upon impact, as shown in Figures 4.13(a) and 4.13(b).

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 have high viscosity upon deposition (see Figures 4.13(c) and 4.13(d)). These particles usually did not show significant concentrations of Na or S.

A test was performed using Upper Hiawatha #1 coal to investigate the extent of deposition and properties of the deposit as affected by physical 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

Figure 4.13. SEM photomicrographs for cross-sectioned adherent material: from high-rank coals (a) Illinois #6 and (b) Pittsburgh #8, showing highly deformed particles; from low-rank coals (c) Powder River Basin and (d) Texas, showing less deformed particles.

Table 4.2, the amount of the deposit formed from the low gas velocity condition was less than that of the deposit formed from the high gas velocity. The appearance of deposit was also different since there appeared only a loosely deposited mass covering the entire substrate surface with no sign of fusing at the upper layer and no adherent layer was noted after brushing off the loosely deposited material. This investigation emphasizes the significant influence of the gas velocity upon the deposit formation process: a drop in gas velocity would result in a decrease in the adhesion force.

In order to reduce any direct radiation on the deposit, the constrictor nozzle was re-designed with the hole cut at a 60° angle to the horizontal. Table 4.2 gives the deposit amounts. The typical appearance of deposit for the three coals tested with this arrangement is shown in Figure 4.14. Figure 4.15 shows the cross-section of a typical deposit from a low-rank coal. As the deposit grows it bends the gas path to pass across the substrate disc, thus leading to deposition of larger particles in the elbow of the deposit, as compared to smaller particles at the opposite side of deposit mass. Pure sodium sulfate crystals were found on the opposite side of the substrate from the deposit mass for Upper Hiawatha #1 and North Dakota lignite. To confirm the existence of sodium sulfate crystals, pure sodium sulfate powder ($\sim 38 \mu\text{m}$) was passed through the furnace under the same experimental conditions: they gave similar shapes and EDS spectra of condensed sodium sulfate crystals as those seen from the coals (see Figure 4.16). The sodium sulfate crystals embedded on the ash particles can be clearly seen in Figure 4.17. The dust material from the Powder River Basin coal contained a mass of needle-shaped

Figure 4.14. Appearance of deposit from N.Dakota lignite
(60° angled constrictor).

Figure 4.15. SEM photomicrographs for cross-sectioned deposit from N. Dakota lignite (60° angled constrictor) (a) at the elbow of deposit; and (b) at the edge opposite to the elbow; showing different size of deposited material between regions (a) and (b); black areas are the impregnated resin.

Figure 4.16. SEM photomicrographs of (a) flaky material from U.Hiawatha #1 coal; (b) flaky material from N.Dakota coal; (c) sodium sulfate crystals from N.Dakota coal; and (d) sodium sulfate crystals from sodium sulfate powder.

Figure 4.17. SEM photomicrographs for (a) sodium sulfate crystals on deposited particle from N. Dakota coal; (b) same as (a) but at higher magnification; (c) sodium-calcium sulfate crystals on deposited particle from Powder River Basin coal; and (d) sodium-calcium sulfate crystal mass at the edge of substrate (Powder River Basin coal).

crystals and the EDS spectra from different areas of the dust material indicated either a combination of calcium and sodium sulfates or calcium sulfates alone. Large particles of deformed calcium sulfate were found in the elbow of the deposits from North Dakota lignite and Powder River Basin coal, as shown in Figure 4.18. In addition, there were a number of particles (dermaspheres) which had high Ca EDS peaks (plus some Fe, Al, Si, and Ti) in the center of the particles but no S, plus a layer of calcium sulfate on the outside (see Figure 4.19). The deposit from North Dakota lignite had more of this type of particle. Apart from these occurrences, cross-sectioning and SEM-EDS analysis of the deposit masses from the tested coals showed essentially the same structures as seen previously.

4.3.2 Slag Deposit Formation from Several Synthetic Coals

The composition, size distribution, and ash fusion temperatures of the synthetic coals are given in Tables 4.8(a) and 4.8(b). The results of deposit mass and percent ash recovered as deposit are shown in Table 4.9. Figure 4.20 shows a typical physical appearance of the deposits from the synthetic coals. Figure 4.21 consists of SEM photomicrographs of structures at different locations on these deposits: (1) the dust material; (2) the lower portion of the deposit mass; (3) the upper portion of deposit mass; (4) the top portion of the deposit mass; (5) the adherent material at the interface between the deposit and the steel substrate after brushing off the loose ash; and (6) the collected fly ash using the pipe/cyclone ash collector probe. The qualitative structure of the deposits at various locations is given in Table 4.10. Most of the deposits grew in a manner similar

Figure 4.18. SEM photomicrograph of cross-sectioned adherent material at the elbow region; (a) deposit from N. Dakota lignite coal (60° angled constrictor) and (b) the corresponding S mapping.

Figure 4.19. SEM photomicrographs for cross-sectioned adherent material at the elbow region; deposit from N.Dakota lignite (60° angled constrictor); (a) dermaspheres at the interface; and (b) dermaspheres in the higher layer of deposit.

Table 4.8(a). Size distributions of test materials from synthetic coals.

Sieve size, μm	Cumulative weight percent less than size					
	80%polymer +20%pyrite	80%polymer +20%illite	80%polymer +20%quartz	80%polymer +15%pyrite +5%illite	80%polymer +15%pyrite +5%kaolinite	80%polymer +15%pyrite +5%quartz
250	100.0	100.0	100.0	100.0	100.0	100.0
210	82.9	86.5	87.7	87.4	77.6	82.4
149	49.9	49.7	59.9	52.2	47.9	54.8
105	27.0	24.7	37.0	28.0	22.2	32.2
74	10.8	7.6	18.4	11.3	12.1	15.2
53	2.8	2.6	17.5	4.3	5.0	9.8
44	0.0	0.0	0.0	0.0	0.0	0.0

Table 4.8(b). ASTM fusion temperatures of synthetic coal ashes,^{*}°C.

Material (wt%)	Oxidizing atmosphere				Reducing atmosphere			
	ID	ST	HT	FT	ID	ST	HT	FT
80%polymer+20%pyrite	1470	1470	1470	1470	1190	1190	1200	1200
80%polymer+20%illite	1290	1310	1350	1380	1210	1240	1270	1340
80%polymer+20%quartz	>1500	>1500	>1500	>1500	>1500	>1500	>1500	>1500
80%polymer+15%pyrite+5%illite	1430	1430	1440	1450	1110	1110	1120	1130
80%polymer+15%pyrite+5%kaolinite	1400	1410	1410	1420	1120	1140	1150	1160
80%polymer+15%pyrite+5%quartz	>1500	>1500	>1500	>1500	1140	1160	1160	1170
Synthetic Illinois #6 coal	1250	1270	1350	1370	1040	1060	1140	1200
Illinois #6 coal	1280	1300	1350	1390	1090	1120	1140	1180

* high temperature ash(ASTM).

Table 4.8(c). Proximate and ultimate analysis of the synthetic Illinois #6 coal.*

Proximate analysis (wt.%)

Moisture	3.0
Volatile matter	79.1
Ash content	17.1
Fixed carbon	4.0

Ultimate analysis (wt.%)

Carbon	56.1
Hydrogen	4.9
Nitrogen	6.2
Sulfur	2.6
Ash	17.1
Oxygen (difference)	13.1

Note; Values (other than moisture) are on a "dry" basis.

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

Table 4.9. Deposits and collected fly ashes from synthetic coals: 10 g material in 30 minutes.

Synthetic material (wt.%)	ASTM ash,* %,	Deposit mass,mg	Ash recovered as deposit, %	Collected fly ash mass,mg	Ash recovered as collected fly ash, %
80 polymer + 20 pyrite	11.1	790	71	700	63
80 polymer + 20 illite	19.5	1270	65	782	38
80 polymer + 20 quartz	15.4	15	1	1130	74
80 polymer + 15 pyrite + 5 illite	12.4	920	92	734	60
80 polymer + 15 pyrite + 5 kaolinite	13.6	1260	92	810	60
80 polymer + 15 pyrite + 5 quartz	11.8	160	14	700	60

* high temperature ash (ASTM).

Figure 4.20. Appearance of deposits from synthetic coals: (a) polymer + pyrite; (b) polymer + illite; (c) polymer + quartz; (d) polymer + pyrite + illite; (e) polymer + pyrite + kaolinite; and (f) polymer + pyrite + quartz.

Figure 4.21(a). SEM photomicrographs of deposit from polymer + pyrite: (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top portion of deposit mass.

(a)

(b)

Figure 4.21(a) continued. SEM photomicrographs of (a) adherent material and (b) collected fly ash: both materials from polymer + pyrite.

Figure 4.21(b). SEM photomicrographs of deposit from polymer + illite; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top portion of deposit mass.

Figure 4.21(b) continued. SEM photomicrograph of collected fly ash from polymer + illite.

(a)

(b)

Figure 4.21(c). SEM photomicrographs of deposit from polymer + quartz; (a) material on substrate; and (b) collected fly ash.

Figure 4.21(d). SEM photomicrographs of deposit from polymer + pyrite + illite; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top portion of deposit mass.

(a)

(b)

Figure 4.21(d) continued. SEM photomicrographs of (a) adherent material and (b) collected fly ash: both from polymer+pyrite+illite.

Figure 4.21(e). SEM photomicrographs of deposit from polymer + pyrite + kaolinite; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top portion of deposit mass.

Figure 4.21(e) continued. SEM photomicrographs of deposit from polymer + pyrite + kaolinite; (a) adherent material; (b) cross-sectioned adherent material; (c) collected fly ash.

Figure 4.21(f). SEM photomicrographs of deposit from polymer + pyrite + quartz; (a) dust material; (b) lower portion of deposit mass; (c) upper portion of deposit mass; (d) top portion of deposit mass.

(a)

(b)

Figure 4.21(f) continued. SEM photomicrographs of deposit from polymer + pyrite + quartz; (a) adherent material; (b) collected fly ash.

Table 4.10. Structure of deposits from synthetic coals.

Synthetic material	Dust material	Lower portion of deposit mass	Upper portion of deposit mass	Top portion of deposit mass	Adherent material
80% polymer +20% pyrite	Weak, no sintering, no fusion	Strong, moderate sintering, no fusion	Strong, highly sintering, no fusion	Very strong, fusion (0.2x0.4)	Strong sintering, no fusion
80% polymer +15% pyrite + 5% quartz	"	"	"	Strong, fusion (0.1x0.1)	"
80% polymer +15% pyrite + 5% illite	"	Slightly strong, slightly sintering, no fusion	Strong, highly sintering, no fusion	Strong, fusion (0.2x1.5)	"
80% polymer +15% pyrite + 5% kaolinite	"	"	"	Very strong, fusion (0.4x1.2)	"
80% polymer +20% illite	Weak, sticky, no sintering, no fusion	Slightly strong, moderate sintering, no fusion	"	Very strong, fusion (0.7x1.5)	No adherent material
80% polymer +20% quartz	No dust material	Weak, no sintering, no fusion	Weak, no sintering, no fusion	Weak, no sintering, no fusion	"

to the deposits formed from coals. In addition, the size and shape of the deposited ash particles were comparable with the deposits from coals. The exception is the inorganic material from a synthetic coal containing only quartz which did not melt and adhere to form a deposit, showing that the particles containing quartz did not reach temperatures above the melting point of quartz (1700°C). The mixture of pyrite and quartz again gave a deposit containing only Fe and no Si, showing that quartz did not fuse into the melting pyrite-pyrrhotite system.

The synthetic coal containing only illite formed a large deposit, probably illustrating the importance of a low melting point glass phase forming sticky particles, thus allowing for accumulation and growth of a massive deposit. However, little material adhered after the deposit was brushed off the oxidized steel substrate, indicating that the glassy material from illite was not strongly adhered with the iron oxide layer of the substrate and thus it was not retained on the substrate. Previous results from the sticking test using illite confirmed this conclusion: the sticking temperature of the illite drop was relatively high (450°C) and the adhesion force at 500°C was very weak (~ 2 grams) (Abbott and Austin, 1982). In contrast, the deposit from the synthetic coals containing only pyrite or a mixture containing pyrite and clays gave a significant amount of adherent material. Again, this observation is in agreement with previous results from the sticking test which showed that the sticking temperature of the pyrite droplet was low (250°C) and the adhesion force at 500°C was high (100 grams) (Abbott and Austin, 1982). The adherent material was analyzed and found to be rich in Fe, 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 trace of glassy phase, probably formed from clays, were detected by X-ray diffraction analysis in these deposits, as shown in Table 4.11, suggesting that most of the pyrite but not clays leads to the formation of deposit under these conditions. However, since the composition of iron-rich fly ash contains a small amount of glass, this suggests that this composition was more prone to adhere and sinter resulting in a significant deposit build-up.

A synthetic coal with a starting mineral composition corresponding to Illinois #6 coal was prepared with a mineral mixture of 29% pyrite, 5% calcite, 25% quartz, 5% kaolinite, and 35% illite. Figures 4.22(a) and 4.22(b) compare the SEM photomicrographs of the deposits from the synthetic coal and the actual Illinois #6 coal. These figures show similarity of deposit structure at different locations on the deposits, and the EDS spectra showed the same types of compositions of the deposit spheres. It appears that the presence of calcite caused the fusion of most constituents in the synthetic coal. However, there were some irregular quartz particles that did not fuse into fly ash spheres. The X-ray diffraction results shown in Table 4.11 confirmed these conclusions: at the top of deposit there were phases containing Si and Al (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

Figure 4.22(a). 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 4.22 (a) continued. SEM photomicrographs of (a) adherent material; and (b) collected fly ash from filter; both materials from Synthetic Illinois #6 coal.

Figure 4.22(b). 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 4.22(b) continued. SEM photomicrographs of (a) adherent material; and (b) collected fly ash from filter; both materials from Illinois #6 coal.

Table 4.11. X-ray diffraction analysis of selected deposits and collected fly ash for synthetic coal and Illinois #6 coal; deposit at the top portion of deposit mass; M = major; m = minor; t = trace.

Phase present	Illinois #6 coal	Synthetic Illinois#6 coal	Polymer +pyrite +quartz		Polymer +pyrite +kaolinite		Polymer +pyrite +illite		Polymer +illite	
			<u>deposit</u>	<u>ash</u>	<u>deposit</u>	<u>ash</u>	<u>deposit</u>	<u>ash</u>	<u>deposit</u>	<u>ash</u>
Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$	m	m								
Augite, $\text{Ca}(\text{Fe}, \text{Mg})\text{Si}_2\text{O}_6$	m	m								
Cristobalite, SiO_2					m					
Hematite, Fe_2O_3	M	M	M	m	M	M	M	M		
Glass	M	M			t		t		M	M
Magnetite, Fe_3O_4			m	M	M	M	M	M		
Mullite, $3 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	m								M	
Quartz, SiO_2	M	M	m	m	m	m	m	m	M	M
Spinel, $(\text{Mg}, \text{FeAlO}_4)$	m	M			M	M	M	m		m

coal tested in this furnace.

4.4 Summary

The results obtained in this investigation lead to the following summary:

(1) The gas temperature of 1300°C through the nozzle is at the upper end of temperatures at the exit of a radiant section of a utility boiler furnace, leading to a rapid growth of deposit on the substrate held at 500°C . A coal rate of one-third of a gram per minute for 30 minutes gave deposits from 0.3 to 3 cm in height which could be cross-sectioned and analysed.

(2) The deposits had structures, growth lines, and chemistry similar to those reported for full-scale boiler deposits, with strong sintering and fusion occurring at the top of the deposit exposed to the highest gas temperature.

(3) However, the test conditions used in the vertical externally-heated tube furnace in this study simulated the conditions of boiler wall slagging because of:

- . short particle residence times of 1-2 seconds
- . deposits contained little amount of sodium and sulfur.

(4) Expression of the rate of growth in terms of the variation of ash sticking coefficient with time showed the marked differences in behavior between different coals and between low- and high-rank coals. Under these extreme conditions the ash sticking coefficient approached 1 for some high-rank coals, at the top of deposit. Severely slagging coals showed a strongly accelerated rate of growth, whereas the less severely slagging coals showed a more uniform rate of deposition.

(5) A drop in gas velocity resulted in a decrease in particle-to-particle adhesion force and subsequently minimized deposition, illustrating that gas velocity has a significant influence upon the amount and growth of deposit.

(6) Average particle size in the deposit mass was large, probably indicating deposition by an inertial impaction mechanism, whereas average particle size in the dust material is small, suggesting deposition by particle-diffusion mechanism. The condensation of sodium sulfate involved in the cooled region probably indicated a vapor phase deposition mechanism.

(7) Mounting followed by cross-sectioning of the deposit exposed the interface between the initial layer of particles and the oxide layer on the steel substrate. The initiating particles were strongly bonded to the oxide film. For the high-rank coals most of these particles were deformed, glassy, black and rich in iron. For the low-rank coals these were less deformed, glassy and transparent particles rich in calcium and iron.

(8) Preliminary results of tests using synthetic coals (polymer-mineral mixture) showed that the deposits produced are similar in morphology to deposits produced from coals. The tests using synthetic coals containing pyrite, clays, and quartz showed that the presence of volatile or condensed alkali species was not necessary for deposit formation, at least under the conditions used in this furnace.

(9) Both synthetic coals containing pyrite and pyrite plus clays formed a strong initial deposit layer as well as a build-up of deposit. On the other hand, synthetic coal containing illite grew a

deposit but did not involve a strong initiating layer.

(10) Synthetic coal containing quartz did not melt and adhere to form a deposit. However, if quartz presented in a closed association with any fluxing species in the same particles during combustion, it may form low melting point silicate fly ash particles and subsequently form a deposit (see (11) next). In addition it may be trapped in the molten deposit mass and assimilated in the deposit.

(11) The deposit from a synthetic coal with contained pyrite, clays, quartz and calcite gave a structure and chemistry similar to that from the actual coal with the same ash composition. This showed the role of the calcite, which appears to act as a flux to allow the fusion of pyrite and clays or quartz during combustion.

Chapter 5

STUDIES OF THE PHYSICS AND CHEMISTRY OF THE
DEVELOPMENT OF STRENGTH BY FLY ASH SINTERING5.1 Introduction

As mentioned in the previous chapter, the phenomenon of sintering of fly ash is an important part of the overall deposition process. Several tests were performed in the present study for specifically evaluating the sintering characteristics of fly ash. The approach in this study was to sinter fly ash pellets as a function of temperature, time, and under an oxidizing and a reducing atmosphere to simulate the local conditions at different locations within the deposit. The investigation was then continued by (1) measuring the thermophysical changes (sintered strength and shrinkage) of the sintered products; and (2) following and ascertaining the chemical changes of the sintered products using XRD analysis.

In the first part of this study, sintering of a model system was performed to illustrate a viscous flow mechanism of sintering. Soda-lime-silica glass (soda glass) is a homogeneous material which has been used as a model material to illustrate viscous flow sintering at temperatures near 600°C (Kuczynski, 1949, Kingery et al., 1976, Raask, 1979, and Conn, 1984). On the other hand, fly ash, in particular that from high-rank coal, is a heterogeneous material which is composed of low melting point components (glass material) and high melting point components (crystalline materials) as determined from X-ray diffraction analysis. As a consequence of the difference between the components of soda glass and fly ash, pure soda glass

alone may not be a suitable model material for comparison with the sintering of fly ash. However, a mixture consisting of soda glass powder (low melting point component) and alumina powder (high melting point component) may more closely simulate a fly ash system. In this investigation, the sintering properties of a mixture of soda glass and alumina powder (1:1 by weight) were investigated as a function of temperature. In addition, a system of alumina without soda glass was also tested for comparison. From the results of the compressive strength tests and the associated microscopic structure of the sintered products, the sintering behavior of the mixture of soda glass and alumina powder was compared to the sintering models used in ceramic studies.

In the second part of this study the compressive strengths of two fly ashes were determined as a function of time at various temperatures. The purpose of these tests was to evaluate whether time or temperature could be used to follow the progress of deposit strength. From the results of these tests a decision would be made to fix one of these two variables for further testing. Two fly ashes studied were: (1) Upper Freeport fly ash produced from an Upper Freeport coal (medium bituminous coal from Upper Freeport seam, Pennsylvania); and (2) Beulah fly ash produced from a Beulah lignite coal (Beulah-Zap seam, North Dakota). Both fly ash samples were collected in the bag filter system of a pilot-scale (7 kg/h) pulverized coal combustor (Austin et al., 1983).

In the third part of this investigation, the compressive strength of sintered Upper Freeport fly ash was determined at room temperature and at high temperatures and the results were compared.

The purpose of these tests was to evaluate whether "hot crushing" or "cold crushing" provided the more definitive measurement of an ash deposit strength. This study was expected to help to define the temperature at which ash develops strength on a boiler tube as the deposit grows and as the semi-molten inner layer cools.

In the fourth part of this study, the sintering behavior was evaluated for four fly ashes collected from the 7 kg/h combustor mentioned above. The four fly ashes tested are: (1) Upper Freeport fly ash, produced from a severely slagging mvb-Upper Freeport coal, Upper Freeport Seam, Pa.; (2) Montour fly ash, produced from a moderately slagging mvb-Montour coal, Montour Power Plant, Pa.); (3) Illinois #6 fly ash, produced from a slagging hvb-Illinois #6 coal, River King Mine Seam, Ill.; and (4) Beulah fly ash, produced from a severely fouling Beulah lignite coal, Beulah-Zap Seam, Nd. The reason for these tests was to understand the sintering behavior of fly ashes from these various types of compositions of coals. Analysis of the sintered strength, the chemistry of the sintered products, and the associated analysis of the inorganic constituents in coals was expected to lead to a better understanding of the characteristics and mechanisms of fly ash sintering process. In addition, the behavior of these fly ashes during laboratory sintering were compared with their known performance in utility boilers.

The components identified in the above investigation to contribute most to rapid sintering and provide high strength to the sintered products were studied in the fifth part of this study. Their behavior was verified by adding or extracting of these components in a fly ash followed by determination of strength and analysis of the

sintered products. This information was correlated to the composition of the original fly ash. Solvents such as distilled water and 10% hydrofluoric acid solution were used to extract components, that contribute most to fly ash sintering, from Upper Freeport fly ash. Sodium silicate, calcium silicate, iron silicate, calcium sulfate and kaolinite were added to Upper Freeport fly ash and their sintering behavior were investigated.

In the sixth part of this study, the sintering behavior of four fly ashes were evaluated under reducing conditions (45 volume % CO, 35 % H₂, and 25 % CO₂). The four fly ashes tested were: (1) Upper Freeport; (2) Illinois #6, produced under conditions found in a utility boiler; (3) Illinois #6 gasifier, produced under conditions found in an entrained slagging gasifier; and (4) Beulah. The purpose of these tests was to determine whether atmosphere has a significant effect on the sintering of fly ash. If so, what was its effect and what was the component that contributes most to develop high sintered strength in a reducing atmosphere. Since iron in the reduced state (Fe⁺² and Fe⁰) has been thought to be a critical component in the development of strength in sintered deposits, additives such as hematite (Fe₂O₃) and magnetite (Fe₃O₄) were used to determine their effects on the sintered strength of the Upper Freeport fly ash under oxidizing and reducing atmospheres.

In the final part of this work, the sintering characteristics of a mineral mixture having a composition similar to that of Upper Freeport coal was evaluated. The purpose was to obtain a clearer understanding of the effect of varying the chemical composition relevant to fly ash sintering. It had already been demonstrated that

a mixture of the major minerals found in coals may closely simulate a fly ash system (Conn and Austin, 1984). The mineral mixture used contains 25 wt% quartz, 15 % pyrite, 5 % gypsum, 20 % kaolinite, and 35 % illite. A fused mineral mixture was also tested to study the effect of time-temperature history and the difference in uniformity between the fused and unfused materials on the sintering behavior. Mineral mixture with additives were investigated to identify the components that contribute most to rapid sintering and that are responsible in developing high sintered strength. Additives used in this part of investigation included pyrite, sodium dioxide, sodium silicate, iron silicate, and sodium carbonate coating on the surfaces of the mineral mixture particles.

The effect of a reducing atmosphere on the sintering behavior of a mineral mixture was also investigated. In addition, the behavior of iron during coal ash sintering under oxidizing and reducing atmospheres was evaluated using a mineral mixture containing pyrite and the same mineral mixture without pyrite. Investigation using the mineral mixture included a microexamination of the phases involved in the high temperature transformation and reactions, and a correlation of this information to the measured compressive strength of sintered products.

5.2 Experimental Technique and Procedure

A sintering furnace, as shown in Figure 5.1, had been previously constructed to evaluate coal ash sintering as related to deposit formation in utility boilers (Conn, 1984). The furnace uses electrical resistance to heat samples to temperatures as high as 1300°C,

Figure 5.1. Ash sintering furnace.

at a rate of 6 to 8°C per minute. The heating element is a platinum-40% rhodium wire and is heated by a 120 volt maximum, 10 ampere variable power supply. The sample temperature was measured using a platinum/platinum-10% rhodium thermocouple (type S) attached to the sample crucible. The sintering furnace was used to study fly ash sintering in this study by (1) measuring ash electrical resistance to determine the ash sinter point; and (2) producing a sintered fly ash product whose compressive strength was then measured in an Instron system.

Details on the electrical resistance method to determine the sinter point, such as the theoretical basis, the construction, and the experimental procedure have been described and discussed by Conn (Conn, 1984). Thus only a brief description is given here. To determine the sinter point, the material to be tested was loosely packed (750 kg/m^3) into a small crucible, 10 mm internal diameter and 25 mm high. A disc of platinum foil 10 mm in diameter and 0.5 mm thick was used as an electrode by placing it in the bottom of the sample crucible making contact with another platinum foil disc beneath the sample crucible, as part of an electrical circuit to measure the ash resistance. The platinum electrodes were connected to a 15 volt stabilized d.c. source by way of a 15 to 10,000x1,000 ohm variable resistor in one of the leads, across which a potentiometric recorder was connected. 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, and the slope of this line changes as sintering commences; the temperature at the point where the slope

changes is called the electrical sinter point.

The Barnhart and Williams compressive strength test was modified in the present study by preparing a small 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 heat region takes place (Barnhart and Williams, 1956). To determine the compressive strength, a green pellet was made from 0.12 g of ash mixed with a drop of distilled water and compressed in a die where enough pressure was applied to give a cylinder of 5 mm diameter by 5 mm height having a bulk density of 1200 kg/m^3 . The pellet was put in an alumina crucible of 10 mm diameter and 25 mm height which was subsequently heated in the sintering furnace to the desired temperature at $6-8^\circ\text{C}$ per minute in air, and held at that temperature for a desired time period. The pellet was left inside the furnace to cool to room temperature within approximately 3 hours. The diameter of the cold pellet was measured, and the compressive strength determination was performed using an Instron apparatus.

The compressive strength of the sintered ash pellet can be measured in one of the following ways: (1) at room temperature after removal of the cold sintered ash pellet from the furnace and (2) at high temperature by placing the furnace in the Instron apparatus. To determine compressive strength at room temperature, the sintered pellet was placed on a flat stainless steel plate (3 inch wide, 4 inch long and 0.5 inch thick) in the Instron apparatus and crushed by raising it vertically against the load cell attachment. The load cell can supply loads in the range of 200 to 100,000 lbs. and the output (the force required to crush the sample) was read from a potentiometer

chart recorder. Selected tests were performed in quadruplicate to estimated standard deviations of the experimental reproducibility and several tests were repeated twice to regularly check the reproducibility.

The compressive strength at high temperatures can be determined by placing the furnace assembly in the Instron apparatus. By raising the furnace in the Instron apparatus against the stationary alumina rod and load cell attachment, the load at which the pellet crushed was then obtained. The furnace and the Instron apparatus to determine compressive strength at high temperature is shown in Figure 5.2

For the tests performed in the reducing atmosphere, a gas mixture of 45 volume% CO, 20% CO₂, and 35% H₂ was introduced into and removed from the furnace through the alumina tube assembly (see Figure 5.1). The other exits were sealed with high temperature fiber packing to prevent gas inleakage. The gas flow rate was controlled at approximately 400 cm³ per minute during the warming up, sintering and cooling down periods.

The morphology of the particles of sintered products from the investigations in this study was determined using an ISI DS-130 scanning electron microscope (SEM). X-ray diffraction analysis was performed to identify the phases contained in the as-received fly ashes and the sintered products. A Phillips APD-3600 automated X-ray diffraction unit was used to produce the X-ray diffraction patterns. The details of this apparatus, operation and conditions used in this section had already been described in the previous chapter (see page 130).

Figure 5.2. Instron and sintering furnace arrangement for determining "hot" compressive strength of sintered fly ash.

5.3 Results and Discussion

5.3.1 Reproducibility

Quintruplicate tests on the heat treated pellets of the Upper Freeport fly ash at 1200°C in air were performed in order to estimate standard deviations of experimental reproducibility. The results gave compressive strengths of 35, 34, 34, 35, and 34 MPa. The mean value of the data (34 ± 1) was taken at 95% confidence limits. However, several tests were repeated twice in order to regularly check the experimental reproducibility.

5.3.2 Sintering Characteristics of Soda Glass and Alumina Mixture, and Pure Alumina in Air

Figures 5.3(a) and 5.3(b) are SEM photomicrographs of the alumina powder and the soda glass powder, showing the irregular particle shapes of these materials. The soda glass powder used in this study had a composition of 75 wt.% SiO_2 , 8 wt.% CaO , and 17 wt.% Na_2O and was passed through a 400 mesh sieve (~ 38 micrometers). The size distribution of the alumina powder is given in Table 5.1(b). The ash fusion temperatures of the tested materials are tabulated in Table 5.2.

Figure 5.4 shows the results of the sinter point determination of pure alumina powder, pure soda glass powder, and soda glass plus alumina mixture. The sinter point of pure soda glass powder was 525°C . The pure alumina powder, which has a melting point of 2045°C , gave a sinter point greater than 1200°C . The mixture of soda glass and alumina exhibited a low sinter point at 550°C . This indicates that the properties of soda glass are a determining factor in the

Figure 5.3. SEM photomicrographs of (a) alumina powder; (b) soda glass powder; (c) alumina + soda glass mixture sintered at 950°C in air; (d) alumina + soda glass mixture sintered at 1200°C in air.

Table 5.1(a). 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 5.1(b). 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 5.2. Fusion temperature(^oC) 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.

Figure 5.4. Sinter point determination of : ◇ pure alumina; ○ pure soda glass; □ soda glass and alumina mixture.

sintering process, that is, soda glass became liquid and promoted ionic conduction, resulting in a change in the slope of the $\log R$ versus $1/T$ plot.

Figure 5.5 shows the results of the compressive strength as a function of heat treatment temperature for pure alumina powder and for soda glass plus alumina mixture. There was no development of strength in the heat treatment of pure alumina powder up to the maximum test temperature of 1200°C , whereas the strength of soda glass plus alumina mixture commenced at 800°C and showed a small increase with temperature. This information suggests that soda glass which is a low melting point component in the mixture of soda glass and alumina initiates and enables viscous flow sintering to occur at the low temperatures ($800\text{--}1200^{\circ}\text{C}$). In contrast, no sintering occurred in the system of alumina without soda glass under the same experimental conditions.

Figures 5.3(c) and 5.3(d) are SEM photomicrographs of the cold pellets from soda glass and alumina mixture, showing clearly the glassy phase. The soda glass powder appeared to be liquid at the heat treatment temperature and subsequently solidified as glass during cooling. Since the viscosity of the liquid from soda glass decreases greatly as the temperature increases, it would be reasonable to expect that a high sintering rate, and hence, a high strength could be achieved in such a system (Kingery et al., 1976, and Raask, 1985f). However, the soda glass and alumina mixture investigated in this study gave a relatively low increase in strength with temperature. Figure 5.3(d) shows that the alumina particles remained largely in the same original size and shape while embedded in a glassy matrix of the

Figure 5.5. Compressive strength as a function of temperature for; $\square$ pure alumina; $\circ$ soda glass and alumina mixture.

pellet which was sintered up to 1200°C . This suggests that the alumina particles did not readily dissolve into the liquid phase. The fluid flow properties of the liquid from soda glass associated with the solid grains of alumina particles would have a viscosity greater than the pure liquid. These phenomena suggests that the sintering of the soda glass and alumina mixture in this study displayed a viscous flow with a non-reactive liquid phase mechanism. As a result, a small increase in strength with an increase in temperature was observed.

5.3.3 Effect of Time on Sintering of Fly Ashes in Air

The size distribution, ash fusion temperatures, spectrochemical and mineralogical analyses of the Upper Freeport and the Beulah fly ashes are given in Tables 5.1, 5.2, 5.3; and 5.4, respectively. The effect of time on sintering characteristics of the Upper Freeport fly ash at various temperatures is shown in Figure 5.6(a), where the compressive strength is plotted versus heat treatment time. The fractional change in $(\text{diameter})^2$ was used as a convenient index of shrinkage and expansion of the pellet. Figure 5.7 shows the change in pellet dimensions after cooling, as a function of heat treatment time. The Upper Freeport pellets heated below the sinter point ($<800^{\circ}\text{C}$) did not develop strength, even after holding at the test temperature for several hours. No shrinkage was observed and the pellet remained as a loose powder when removed from the furnace, indicating that no sintering occurred below the sinter point.

The strength of the Upper Freeport pellets heat treated above the sinter point at 950°C and 1000°C increased with time from 15 minutes to 25 hours. It was observed that as the heat treatment

Table 5.3. 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.

Table 5.4. Mineralogical analyses of LTA test coals compared
to U.Freeport mineral mixture.

	U.Freeport coal	Montour coal	Ill.#6 coal	Beulah coal	U.Freeport min. mix.
	Weight %				
LTA	21.6	18.0	22.0	14.1	-
Minerals					
quartz	25	25	25	10	25
pyrite	10	15	29	5	15
calcite	n.d.	5	5	5	-
gypsum	5	n.d.	n.d.	20 ⁺	5
kaolinite	20-30 [*]	20	5	5	20
illite+mixed layer clays	20-40 [*]	30-40 [*]	35 [*]	15-20 [*]	35

@ low temperature ash.

n.d. = not detected.

* estimated value.

+ gypsum may be an artifact of low temperature ashing (LTA)
process when ashing low-rank coals.

Figure 5.6. Effect of time on sintering characteristics of (a) U.Freeport fly ash in air; and (b) Beulah fly ash in air: temperatures are heat treatment temperature.

Figure 5.7. Fractional change in (diameter)² with time for U. Freeport fly ash: Δ 950 °C, $\square$ 1000 °C, $\circ$ 1050 °C, $\odot$ 1150 °C.

temperature increased up to 1000°C , the slope of the compressive strength versus the heat treatment time increased, showing that the rate of sintering increased with temperature. When the pellets were heated at higher temperatures (1050°C – 1150°C), a maximum strength was noted. The higher the heat treatment temperature, the shorter the time for developing the maximum strength. For example, the maximum strength was noted for one hour heat treatment at 1050°C as compared to 15 minutes for heat treatment at 1150°C .

Figure 5.6(b) shows the effect of time on sintering characteristics of Beulah fly ash (sinter point 550°C), at various temperatures. The strength of pellets heat treated from 950°C to 1050°C did not show any significant increase and no shrinkage with time. At higher temperatures (1150°C), however, the strength of pellets increased with time and the pellets underwent some shrinkage. No maximum strength was noted in the sintering of the Beulah fly ash, as compared to that of the Upper Freeport fly ash. The difference in compressive strength of this fly ash as a function of time between the sintering at the low temperatures (950°C – 1050°C) and that at the higher temperature (1150°C), suggests that different mechanisms were possibly involved.

The results of these tests suggest that the sintering time effects the sintering behavior, which is dependent on the heat treatment temperature and the type of coal ash. The fly ash from high-rank coal shows the greater effect as compared to the low-rank coal. This information suggests that different mechanisms probably exist in the sintering process between the fly ashes produced from low-rank and high-rank coals. The results from these tests

illustrated that appreciable strength was achieved using one hour heat treatment time in most tests, hence the one hour heat treatment time was chosen as a sintering time in the further sintering tests as a function of temperature.

5.3.4 Comparison of Strength of Fly Ash Sinters at Room Temperature and at High Temperature

Stress-strain curves for compressive strength tests of Upper Freeport fly ash sintered at 1150^o C for one hour in air are shown in Figure 5.8. The results of tests performed at room temperature are shown in Figure 5.8(a), indicating linear stress with applied linear strain up to ~10% strain, followed by a typical brittle fracture and a sudden large decrease of stress. At 700^o C (see Figure 5.8(b)) 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^o C, the pellet deformed steadily to high strain, leading to a flattened pellet (see Figure 5.8(c)). 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 sinter point and the room temperature test.

Because of the presence of a viscous liquid phase at temperature above the sinter point, the determination of compressive strength at the heat treatment temperature did not result in a

Figure 5.8. Typical stress-strain curves for compressive strength tests for U.Freeport fly ash heated at 1150 °C for 1 hour in air: (a) tested at room temperature; (b) tested at 700 °C; and (c) tested at 1150 °C.

definite strength measurement, but instead resulted in plastic deformation. At the temperature below the sinter point, solidification of this liquid phase and extensive sintered bond formation resulted 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.

5.3.5 Sintering Characteristics of Several Fly Ashes in Air

Fly ashes used in this investigation include three fly ashes produced from high-rank bituminous coals: Upper Freeport, Montour, and Illinois #6, and a fly ash produced from a low-rank Beulah lignite. The size distribution, ash fusion temperatures, spectrochemical and mineralogical analyses of these fly ashes are tabulated in Tables 5.1(a), 5.2, 5.3, and 5.4, respectively.

Figure 5.9 shows the results of sinter point determination of all tested fly ashes. The sinter point of Upper Freeport and Montour fly ash were identical (800°C), whereas Illinois #6 fly ash exhibited a sinter point at 725°C . Of all the tested fly ashes Beulah fly ash showed by far the lowest sinter point at 550°C . However, the strength of the Beulah fly ash commenced at 400°C above the sinter point (see Figure 5.10). According to the X-ray diffraction analysis, the as-received Beulah fly ash contained significant amount of sodium and mixed alkali sulfates. These phases have low melting points that would give liquid ionic conduction at the low temperatures and cause a change in the slope of $\log R$ versus $1/T$ plot. It is suggested from

Figure 5.9. Determination of fly ash sinter point by electrical resistance measurement: $\circ$ Illinois #6 fly ash; $\square$ U. Freeport fly ash; $\square$ Montour fly ash; $\circ$ Beulah fly ash.

Figure 5.10. (a) Compressive strength and (b) the corresponding fractional change in (diameter)² as a function of temperature for U.Freeport fly ash (○), Montour fly ash (□), Illinois #6 fly ash (△), and Beulah fly ash (⊙).

the low sinter point (550°C) but the high temperature (950°C) necessary for developing strength of the Beulah fly ash that the change in slope of the plot 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. Beulah fly ash exhibited a lower electrical resistance as compared to that of the other tested coals: this was thought to be because of the presence of significant amount of a conductive ionic specie, probably sodium-based. For the fly ashes from high-rank coals that contain only traces of the alkali and mixed alkali sulfate phases, 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 $100\text{--}200^{\circ}\text{C}$ above their sinter points. Most of the heat-treated fly ashes at their sinter points remained as a loose powder when removed from the furnace.

Figure 5.10(a) shows the relationship between the cold pellet strength and heat treatment temperature for all the fly ashes tested. Upper Freeport, Montour and Illinois #6 fly ashes showed a maximum in strength development, whereas Beulah fly ash showed a small increase in strength with temperature. The change in pellet dimension as a function of heat treatment temperature, after cooling to room temperature for all the fly ashes tested, is shown in Figure 5.10(b). It can be seen that the maximum in strength of these fly ashes corresponded to a maximum in shrinkage, and the pellet expanded as strength fell after the maximum strength. No dimensional change was observed in Beulah fly ash pellets except that of the pellet heat-treated at 1150°C . The color of these pellets was generally

yellow-brown and became darker with increasing temperature.

SEM photomicrographs of Upper Freeport sintered pellets after cooling are shown in Figure 5.11. The development of sinter necks and the formation of a glassy phase are clearly indicated. The maximum strength appears to be related to the greatest glass content in the pellet. The phases determined by XRD of the as-received Upper Freeport fly ash shown in Figure 5.12 revealed that it contained significant amounts of glass material plus crystalline material such as quartz (SiO_2), hematite (Fe_2O_3), and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

The probable explanations for the sintering behavior of the Upper Freeport fly ash which shows a characteristic of rise and fall of strength with temperature is as follows. At the temperature that strength development commenced ($\sim 850^\circ\text{C}$), the low melting point glass material originally present in the as-received fly ash formed a liquid phase, enabling viscous flow sintering to occur. As the heat treatment temperature increased, the high temperature in the pellet lowered the viscosity of the liquid phase. In addition, the liquid content probably increased from the melting of higher melting point glass material and by dissolution of other high melting point ash components into the liquid phase. This resulted in the shrinkage of small particles followed by the growth of the larger ones, producing a structure of coalescence of round grains surrounded by a liquid (see Figure 5.11(c)). 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 diffusion coefficient of mass transfer in liquid. The resulting matrix had a very high strength due to the liquid phase which produced a glass on cooling and gave associated

Figure 5.11. 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 °C, (c) sintered at 1050 °C; and (d) sintered at 1200 °C.

X-ray Intensity

Figure 5.12. X-ray diffraction patterns of U.Freeport fly ash; (a) as received fly ash; (b) sintered at 1000 °C for 1 hour in air; (c) sintered at 1050 °C for 1 hour in air; and (d) sintered at 1200 °C for 1 hour in air; only major crystalline peaks were labelled as Q = quartz, M = mullite, F = hematite, broad background indicated amorphous or glass.

extensive sintered bond formation in the heat treated pellet.

The decrease in strength and reversal of shrinkage of the Upper Freeport pellet at the higher heat treatment temperatures ($>1050^{\circ}\text{C}$) was observed to be associated with the formation of crystalline phases. The content of crystalline phase appears to increase with temperature. Gradual decrease in the glass content, as indicated by a reduction in the XRD broad background, was observed at temperatures greater than 1050°C (see Figure 5.12). The crystalline phase is clearly indicated in the SEM photomicrographs shown in Figure 5.11(d) and it was detected by XRD to be mullite. Although a small amount of mullite was originally present in the as-received fly ash, the greater content of mullite formed at the higher temperatures ($>1050^{\circ}\text{C}$) could be the result of thermal decomposition products of the aluminosilicate glass material contained in the as-received fly ash. This implies that some of the bonding glass was removed from the sintering mass. The heat treated pellet which was removed hot from the furnace and rapidly cooled below the sinter point within one minute, still showed the presence of mullite crystals, but it had more glass content. Since mullite has a melting point of 1810°C , the formation of mullite during sintering would remain in a crystalline solid phase at the heat treatment temperatures ($900\text{--}1200^{\circ}\text{C}$). The reduction in strength of the fly ash at high temperatures ($>1050^{\circ}\text{C}$) thus is due to the reduction of the bonding glass phase by transformation of the glassy phase into crystalline phase, which raises the viscosity of the residual liquid, and hence reduces the rate of sintering.

A decrease in quartz content was noted in the XRD patterns of the Upper Freeport pellets heat treated at high temperatures,

suggesting that it probably dissolved into the liquid phase. Its effect on the sintering rate, however, was not clear. It may be speculated that the dissolution of quartz might not have a great effect on the amount or composition of the liquid phase, because the liquid was normally highly siliceous. On the other hand, it was noted that the intensity of hematite peaks in the XRD patterns remained virtually unchanged with temperature, indicating that iron (III) oxide does not participate in the sintering process, probably due to the fact that the fly ash already contained the iron aluminosilicate or iron silicate glass components necessary for sintering. It is tentatively concluded that the glass material originally present in the as-received Upper Freeport fly ash promotes deposit strength with temperature by forming the liquid phase and initiating the viscous flow sintering. The major factor causing a reduction of the sintering rate at higher temperatures was likely to be the production of additional mullite crystals which changed the composition, amount, and viscosity of the liquid bonding phase.

Montour fly ash developed higher strength at temperature range of 850°C to 1000°C but at temperature greater than 1000°C it had a lower maximum strength than Upper Freeport fly ash, even though the chemical analysis of these two fly ashes were very similar (see Figure 5.10). Figure 5.13 shows SEM photomicrographs of Montour sintered pellets after cooling. Higher glassy phase content was observed in the XRD pattern of the Montour sintered pellet (see Figure 5.14(b)) as compared to that of the Upper Freeport (see Figure 5.12(b)) at the same heat treatment temperature of 1000°C . The high glass content in Montour fly ash would indicate that large amounts of liquid phase

Figure 5.13. SEM photomicrographs for the structure of the cold pellets from Montour fly ash, as a function of temperature (1 hour, in air); (a) as received fly ash (after burn off carbon); (b) sintered at 900 °C; (c) sintered at 1000 °C; and (d) sintered at 1100 °C.

Figure 5.14. X-ray diffraction patterns of Montour fly ash; (a) as received fly ash; (b) sintered at 1000 °C for 1 hour in air; (c) sintered at 1050 °C for 1 hour in air; and (d) sintered at 1100 °C for 1 hour in air; only major peaks were labelled as Q = quartz, M = mullite, F = hematite, and A = anorthite.

formed. Enough liquid phase would bring most of the particles together and fill most of the pores causing sintering to take place rapidly. This may account for the higher strength of Montour sintered pellets developed at lower temperatures (850-1000°C) than those of Upper Freeport under these conditions.

However, it was observed that the formation of crystalline phase in the Montour pellet again appears to correspond to the reduction in strength at high temperatures (>1000°C). The major crystalline phases identified by XRD were anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and mullite. The amount of these crystalline phases increased with temperature, whereas glass and quartz gradually lessened. Although the Montour fly ash contained 2.3 wt% calcium, which is comparable to that contained in the Upper Freeport fly ash, it is possible that a larger content of liquid formed from the high glass constituent in Montour fly ash. This liquid could spread over the surface of adjacent particles, thereby increasing the effective surface for chemical reaction of calcium with aluminosilicate glass to form anorthite crystals. As a consequence, the sintered product of Montour fly ash contained a high concentration of crystalline phases of both anorthite and mullite, whereas the sintered product of Upper Freeport contained only mullite at high temperatures (>1050°C). The greater concentration of crystalline phases in the sintered products heat treated at the high temperatures from Montour fly ash thus may account for the lower maximum strength as compared to the Upper Freeport fly ash. The sintering behavior of Upper Freeport and Montour fly ash appears to be in accord with the utility experience using these two coals, since Montour coal gives less problems with upper furnace

sootblowing operation than Upper Freeport coal (Tice, 1980).

Fly ash from Illinois #6 coal showed the same characteristic rise and fall of strength with temperature but gave the lowest maximum strength as compared to the other tested fly ashes from high-rank coals (see Figure 5.10). Figure 5.15 shows SEM photomicrographs of cold sintered pellets from Illinois #6 fly ash. The glassy phase was clearly indicated in the sintered pellet of this fly ash at the heat treatment temperatures from 900°C to 1000°C . However, a significant amount of crystalline phases formation occurred at temperatures as low as 1000°C , probably due to the relatively high content of calcium in Illinois #6 fly ash that would readily interact with the aluminosilicate glassy phase to form a crystalline phase of anorthite. This would readily remove the bonding glass and reduce the strength of the pellets at elevated temperatures. The XRD patterns of the as-received fly ash and their sintered products are shown in Figure 5.16. The mullite peaks in the XRD pattern of the as-received Illinois #6 fly ash could not be clearly discerned, suggesting that the original clay structure was present largely as an amorphous glass material in the as-received fly ash. The development of mullite crystals at high temperatures ($>1050^{\circ}\text{C}$) was not observed, suggesting that the bonding glass was largely removed by forming the anorthite phase. The system which contained anorthite, but not mullite appeared to cause the pellet to deform at a low temperature (1100°C). This appears to be in accord with the relatively lower initial deformation temperature (IDT) of Illinois #6 ash as compared with the other ashes from high-rank coals (see Table 5.2).

The rate of sintering is high for the fly ashes from high-rank

Figure 5.15. SEM photomicrographs for the structure of cold pellets from Illinois #6 fly ash, as a function of heat treatment temperature for 1 hour in air; (a) as received fly ash (after carbon burn-off); (b) sintered at 950°C; (c) sintered at 1050°C; (d) sintered at 1150°C.

Figure 5.16. X-ray diffraction patterns of Illinois #6 fly ash; (a) as received fly ash; (b) sintered at 1050 °C for 1 hour in air; (c) sintered at 1150 °C for 1 hour in air; only major peaks were labelled as Q = quartz, F = hematite, S = CaSO_4 , and A = anorthite.

coals at the heat treatment temperatures from 900°C to 1050°C . For example, the strength of the Upper Freeport fly ash changed by a factor of ten over an interval of 200°C (950°C - 1050°C) and the maximum shrinkage changed by 40 percent. Sufficient evidence exists to indicate that the sintering involves the formation of a bonding liquid phase from the glass material in the original fly ash, that the content of liquid phase increases with temperature and there is a dissolution of the solid components into the liquid. It is suggested from this information that the sintering of fly ash from high-rank coals involves a viscous flow with a reactive liquid phase mechanism, under these conditions (sintering temperature range 850 - 1050°C ; 1 hour heat treatment temperature in air).

However, at temperatures greater than 1050°C the sintering behavior of the fly ashes from high-rank coals is complicated by the production of the new crystalline phases which form due to phase decomposition and chemical reactions. The newly formed crystalline phases reduce the amount of the bonding liquid, increase the viscosity of the bonding liquid, and change the composition of the bonding liquid, resulting in reduction in strength of the sintered pellets. The newly formed crystalline phases (mainly mullite and anorthite) have high melting points and the content of crystalline phases increases with temperature. The evidence indicates that the crystalline phases do not readily dissolve in the liquid phase at the test temperature, showing that the sintering of fly ash from high-rank coals involves a viscous flow with a non-reactive liquid phase mechanism under these conditions.

Thus, there probably exists two viscous flow mechanisms

involved 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°C). 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 fly ash from Beulah lignite exhibited a different behavior as compared with those of the fly ashes from high-rank coals (see Figure 5.10). Only a small increase in strength with temperature was observed in the sintering of Beulah fly ash. No maximum strength and no shrinkage occurred until the heat treatment temperature of 1150°C. Figure 5.17 shows SEM photomicrographs of the cold sintered pellets from Beulah fly ash. Crystalline phases in the sintered products were predominant over the glass material in the as-received fly ash as indicated in the XRD patterns in Figure 5.18.

The crystalline phases that formed at 950°C include the melilite series of minerals; gehlinites ($\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7$), sodium melilite ($\text{Na,CaAlSi}_2\text{O}_7$) and nepheline (NaAlSiO_4). These minerals contain calcium and sodium cations within a silica-deficient aluminosilicate structure. These crystalline phases form where there is an abundance of alkalis (Na,K), alkali earth (Ca) and a lack of silica. As the heat treatment temperature increased, the XRD peaks of the melilites increased in intensity. In addition, the sodalite type minerals; hauyne ($\text{Na,Ca}_{4-8}(\text{Al}_{12}\text{Si}_{12}\text{O}_{24})(\text{SO}_4)_4$) and nosean ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)_4$) were identified. These phases are similar to the melilites, but contain minor sulfate concentrations and have lower melting points (Goblirsch et al., 1983). Formation of the melilites and the

Figure 5.17. SEM photomicrographs of Beulah fly ash; (a) as received fly ash (after carbon burn-off); (b) sintered at 950°C for 1 hour in air; (c) sintered at 1100°C for 1 hour in air; (d) sintered at 1150°C for 1 hour in air.

Figure 5.18. X-ray diffraction patterns of Beulah fly ash; (a) as received fly ash; (b) sintered at 950°C for 1 hour in air; (c) sintered at 1050°C for 1 hour in air; and (d) sintered at 1150°C for 1 hour in air; only major peaks were labelled as Q = quartz, S = Na_2SO_4 , F = hematite, D = MgO, P = spinel (MgFe_2O_4), G = gehlenite, H = haulyne, N = nosean, B = akermanite, L = nepheline, and E = sodium melilite.

sodalites are thought to be the result of complex reactions between alkalis, alkali earth, sulfates and aluminosilicates (Rindt et al., 1981, and Deer et al., 1963). In order to determine whether these crystalline phases exist at the heat treatment temperature a heat treated pellet (at 1200°C in air) was quickly removed from the hot furnace and cooled below the sinter point in about one minute. The rapidly cooled material still showed the crystalline phases quite similar to those obtained in the slowly cooled pellet.

Significant amounts of glass material and alkali sulfates were detected in the XRD pattern in the as-received Beulah fly ash (see Figure 5.18(a)). Accordingly, these materials would provide a liquid phase enabling sintering to occur. However, it may be possible that some of the liquid phase formed at the heat treatment temperature was quickly removed by interaction of the abundant alkalis, alkali earth, sulfates and aluminosilicate glass to form crystalline phases. It appeared, therefore, that the strength of these pellets resulted mainly from the properties of the newly formed crystalline phases, that is, it was due to the formation of crystalline bridges between particles. The strength of Beulah fly ash changes by a factor of one to two over an interval of 200°C (from 950°C-1050°C) and there was virtually no shrinkage observed in these heat treated pellets, indicating that the rate of sintering was low. The crystalline phases (mainly melilites) have high melting points and their amounts increased with strength and temperature, indicating these phases did not readily dissolve in the liquid phase. It is suggested from this information that the sintering of fly ash from low-rank coals displays a viscous flow with a non-reactive liquid phase mechanism under these

conditions (sintering temperature 850-1150^o C; 1 h heat treatment in air).

The sintering behavior of the Beulah fly ash at higher temperatures (>1150^o C) showed higher strength and higher shrinkage than at lower temperatures. In addition, the hot crushing test of the Beulah pellet showed plastic deformation, suggesting that a substantial amount of liquid forms at the high temperatures (>1150^o C). The probable cause of the increase in liquid content at high temperatures can be the melting of some of the crystalline phases formed during heating up of the pellet. The sintering proceeds more rapidly with the dissolution of the solid, and matter transports by diffusion through the liquid. The viscous flow with a reactive liquid phase, therefore is a predominant mechanism in the sintering process of the Beulah fly ash at higher temperatures (>1150^o C). It was noted that once the liquid phase was present at the high temperatures the pellet readily deformed, indicating that most of the crystalline phases dissolved into the liquid. This appears to be in accord with the fusion behavior of this ash that occurs in a narrow range of temperature (~50^o C) (see Table 5.2).

Melilites and sodalites have been found in the deposits formed in boilers when firing with the high sodium low-rank coal (Rindt et al., 1983, Mazza and Wilson, 1977). As a consequence, these investigators believed that the strength resulting from these crystalline properties makes bonded deposits in boilers difficult to remove on-load. Although the results from this study were found in accord with these investigators, 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 (fouling) deposit in boilers. In boilers there is a constant stream of alkali and sulfur oxide vapors in the flue gases which passes through the bonded deposit. These would develop sufficient liquid phases from sodium and mixed alkali sulfates, sodium melilite, and sodalites in the deposit matrix which would enhance sintering rate and, hence, would make the bonded deposit harder and stronger than it was observed in this investigation.

5.3.6 Sintering Behavior of Fly Ash after Extraction and Addition of Glass Materials in Air

The sintering behavior of several fly ashes from high-rank coals described in the previous section involved a viscous flow mechanism of the bonding glassy phases that formed from the glass material in the as-received fly ash. Change in the composition of the glass material in the fly ash thus would affect the sintering process, that is, the rate of sintering can be lowered by reducing the glass content of the fly ash and vice versa. To test this hypothesis the water-soluble glass material was extracted out of Upper Freeport fly ash by dissolving it in distilled water.

Figure 5.19 shows the results of the sinter points of the water-washed Upper Freeport fly ash and the unwashed fly ash. The sinter point of water-washed fly ash was 850°C which was 50°C higher than the unwashed fly ash. Figure 5.20 shows the effect of water washing on the sintered strength of fly ash as a function of heat treatment temperature. The water washing removed some of the low melting point components and hence, the resultant sintered product had

Figure 5.19. Sinter point determination for; ○ Upper Freeport fly ash; ◇ water-washed Upper Freeport fly ash; □ HF-washed Upper Freeport fly ash.

Figure 5.20. Compressive strength as a function of temperature for; ○ Upper Freeport fly ash; □ water-washed Upper Freeport fly ash; ◇ HF-washed Upper Freeport fly ash.

a lower maximum strength, as compared to the unwashed fly ash sinter. At higher temperatures ($>1100^{\circ}\text{C}$) there was still a reduction in strength, as that observed from the unwashed fly ash. Table 5.1(a) (see page 228) shows the size distribution of the water-washed fly ash: it appears that the washing removed fine particles. The phases identified in the XRD patterns of the water-washed fly ash and the sintered pellets, as shown in Figure 5.21 were similar to those of the unwashed material (see Figure 5.12). This information indicates that the water washing had removed only a small fraction of water-soluble-low melting point glass, but a large fraction of glass component which is a water-insoluble material and contribute most to sintering process still remained in the water-washed fly ash.

A diluted hydrofluoric acid solution (10%) was used to remove most of the glassy phases from the Upper Freeport fly ash. The size distribution of the HF-washed fly ash is given in Table 5.1(a) (see page 228). The SiO_2 , CaO , K_2O , and Na_2O contents were reduced as noted from the spectrochemical analysis of the HF-washed fly ash compared to the unwashed fly ash (see Table 5.3). The XRD patterns are illustrated in Figure 5.23(b), showing a smooth, well defined background, indicating little glass material contained in the HF-washed fly ash as compared to the broad background of the glass material in the unwashed fly ash (see Figure 5.23(a)). The HF-washed fly ash contained crystalline phases of mullite, hematite, magnetite, and some spinels ($\text{Mg,FeAl}_2\text{O}_4$).

Figure 5.19 shows the results of sinter point determination of both the HF-washed fly ash and the unwashed fly ash. The sinter point of the HF-washed fly ash was 1025°C which was 225°C higher than that

Figure 5.21. X-ray diffraction patterns of water-washed U. Freeport fly ash; (a) as water-washed fly ash; (b) sintered at 950 °C for 1 hour in air; (c) sintered at 1050 °C for 1 hour in air; and (d) sintered at 1200 °C for 1 hour in air; only major peaks were labelled as Q = quartz, M = mullite, and F = hematite.

of the unwashed fly ash, showing that the sintering commences at higher temperatures. Figure 5.20 shows the effect of HF-washing on the sintered strength of fly ash as a function of temperature. Below 1150°C the pellet did not develop appreciable strength and exhibited no shrinkage, no color change and no difference in the XRD patterns. At 1150°C , however, the HF-washed pellet exhibited small strength and a shrinkage, indicating that sintering had occurred at this temperature. In addition, glassy phases and traces of anorthite and gehlenite were present. Disappearance of mullite and quartz peaks were also observed. This is clear evidence that the high temperature (1150°C) produced enough reaction to start forming the glassy and crystalline phases from the interactions between the components of the HF-washed fly ash. The newly formed phases may account for the development of strength at the high temperature (1150°C).

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 5.22(a) shows the appearance of the HF-washed fly ash: the surfaces of particles were etched revealing the roughness of crystalline skeletons, probably mullite. The lack of the glass material on the surfaces of the HF-washed fly ash particles, which produced the weak deposit, indicated that sintering occurs at the surface of most fly ash spheres.

Results from the strength test of the HF-washed fly ash sinters agree well with the hypothesis that the glass material in the fly ash promotes deposit strength. However, there are several types of species

Figure 5.22. 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 $^{\circ}\text{C}$ for 1 hour in air; (c) sintered at 1100 $^{\circ}\text{C}$ for 1 hour in air; and (d) sintered at 1150 $^{\circ}\text{C}$ for 1 hour in air.

Figure 5.23. X-ray diffraction patterns of HF-washed U. Freeport fly ash; (a) as received fly ash; (b) as received HF-washed fly ash; (c) sintered at 1000 °C for 1 hour in air; and (d) sintered at 1150 °C for 1 hour in air; only major peaks were labelled as Q = quartz, M = mullite, F = hematite, B = magnetite, G = gehlenite, and A = anorthite.

that can be associated with the glasses. To identify these species in the glass material, various silicate glass compounds containing sodium, calcium, and iron in the pulverized form were added to the fly ash before making a pellet. A sodium silicate glass was prepared by melting a mixture of 30 wt% sodium carbonate and 70 wt% quartz at 1750°C in a methane-oxygen flame. The cooled glass was hand pulverized to a fine size (~ 15 micrometers), and 10 wt.% of the additive was mixed with the fly ash before making the pellets. Calcium silicate was made in a similar fashion from 30 wt% calcite (CaCO_3) and 70 wt% quartz and iron silicate was produced from 30 wt% pyrite (FeS_2) and 70 wt% quartz. These additives were ground to the size distribution given in Table 5.1(b) (see page 229).

Addition of sodium silicate into Upper Freeport fly ash reduced the sinter point of the fly ash to 650°C , whereas the other additives decreased the sinter point of the fly ash to 725°C . Figure 5.24(a) shows the effect of sintered strength when sodium silicate was added to Upper Freeport fly ash. This additive led to the development of higher strength at lower temperatures ($850\text{--}1000^{\circ}\text{C}$), but the strength started to reduce after the temperature reached 1025°C and the pellet deformed at 1100°C . It is possible that sodium silicate could provide additional low melting point material and lowered the viscosity of liquid phase in the fly ash at lower temperatures ($<1025^{\circ}\text{C}$). The high concentration of the sodium species could also react with aluminosilicate glass to form crystalline phases, resulting in the reduction of the maximum strength and the deformation of the pellet at high temperatures ($>1025^{\circ}\text{C}$). However, except for the presence of cristobalite, there appeared no significant difference crystalline

(a)

(b)

Figure 5.24(a). Compressive strength versus heat treatment temperature (for 1 hour, in air) of Upper Freeport fly ash (○) and Upper Freeport with addition of (a) sodium silicate (□);(b) calcium silicate (□) and calcium sulfate (◇).

phases identified in the XRD patterns, as shown in Figure 5.25, between that of the Upper Freeport fly ash without or with sodium silicate, probably due to the presence of great amount of amorphous glass in both systems.

The calcium silicate additive behaved similarly to that of sodium silicate at low temperatures (850-950°C), but the calcium specie appeared to react readily with the aluminosilicate glass in the fly ash to form anorthite crystalline phase at temperatures as low as 1000°C (see Figure 5.26). This may account for the lower maximum strength, as compared to the Upper Freeport fly ash (see Figure 5.24(a)). Another form of calcium (calcium sulfate) added to the fly ash was also investigated. The result is also shown in Figure 5.24(a). Calcium sulfate was more effective in reducing the strength of the sintered fly ash than calcium silicate. At a temperature of 950°C, a significant amount of calcium sulfate was detected in the XRD pattern, as shown in Figure 5.27, indicating that calcium sulfate did not decompose and had no effect on the sintering behavior of the fly ash. At 1000°C, however, the intensity of the calcium sulfate peaks started to decrease, whereas anorthite was identified, showing that calcium sulfate decomposed to calcium oxide which was then reacted with aluminosilicate glass to produce anorthite. As the temperature increased, calcium sulfate and quartz disappeared, whereas anorthite increased, and these phenomena appeared to be associated with the reduction of strength. Crystalline phase containing sulfur was not detected: probably it was driven out of the pellet as gas or it might be retained in the pellet in the amorphous phase. The mullite intensity peaks appeared smaller than that of the fly ash without

(a)

(b)

Figure 5.24(b). Compressive strength versus heat treatment temperature (for 1 hour, in air) of Upper Freeport fly ash (○) and Upper Freeport fly ash with addition of (a) iron silicate (◻) and (b) kaolinite (◻).

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Figure 5.25. X-ray diffraction patterns of U. Freeport fly ash plus sodium silicate additive; (a) sintered at 950°C for 1 hour in air; (b) sintered at 1050 °C for 1 hour in air; and (c) sintered at 1100 °C for 1 hour in air; only major peaks were labelled as Q = quartz, M = mullite, C = cristobalite, and F = hematite.

Figure 5.26. X-ray diffraction patterns of U.Freeport fly ash plus calcium silicate additive; (a) sintered at 1000 °C for 1 hour in air; (b) sintered at 1050 °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; only major peaks were labelled as Q = quartz, M = mullite, A = anorthite, F = hematite.

Figure 5.27. X-ray diffraction patterns of U.Freeport plus calcium sulfate additive; (a) sintered at 950°C for 1 hour in air; (b) sintered at 1000 °C for 1 hour in air; (c) sintered at 1050 °C for 1 hour in air; and (d) sintered at 1150 °C for 1 hour in air; only major peaks were labelled as Q = quartz, M = mullite, F = hematite, A = anorthite, and C = calcium sulfate.

additive, suggesting that much of the glass was probably removed by forming anorthite.

Raask studied the reaction between calcium sulfate and ash at ash sintering temperatures by monitoring the weight loss of this reaction in air at the rate of 6°C per minute using a thermogravimetric measurement (Raask, 1984). He observed that there was a weight loss of calcium sulfate/ash (1:1 by weight) at 1000°C , whereas calcium sulfate alone showed signs of weight loss only after 1300°C . The temperature at which the calcium additive reacts with ash components to reduce strength in the present study agreed with the Raask's observation. Calcium in the form of calcium carbonate was shown to be an effective additive for reducing deposit strength in a large-scale boiler (Honea, 1983).

Addition of iron silicate had virtually no effect on the strength of the fly ash, as shown in Figure 5.24(b), indicating that the fly ash already contained sufficient iron glass components for sintering. The XRD patterns of both the fly ash with or without iron silicate appeared to be similar, except for the presence of cristobalite (see Figures 5.12 and 5.28), indicating that the iron species did not undergo devitrification to form crystalline phases, that is, iron did not reduce the bonding glassy phases in the fly ash. The results of these tests indicated that calcium greatly lowered the maximum strength of the fly ash, whereas sodium had little effect and iron had no effect. This implies that calcium is generally not a component that contributes most to the formation of strong deposit, whereas sodium and iron do, at least under the conditions used in this study.

Figure 5.28. X-ray diffraction patterns of (a) iron silicate glass; and U.Freeport fly ash plus iron silicate sintered for 1 hour in air at (b) 950 °C; (c) 1050 °C; and (d) 1150 °C; only major peaks were labelled as Q = quartz, C = cristobalite, M = mullite, and F = hematite.

Addition of kaolinite to Upper Freeport fly ash was also tested. Figure 5.24(b) shows that kaolinite gave no effect up to the heat treatment of 1050°C , but caused a higher strength at higher temperatures (1025 – 1175°C). This indicated that the thermally decomposed kaolinite phase did not participate in developing strength at a low temperature range (850°C – 1050°C), but between the temperatures of 1025°C – 1175°C the higher temperatures produced enough reaction to begin forming the bonding glassy phase. The additional amount of the bonding phase would raise the rate of sintering under these conditions. At temperatures greater than 1100°C , however, the bonding glass probably thermally transformed to mullite which raised the viscosity of the residual glass and thus caused a reduction in strength.

The above 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. From an understanding of the sintering behavior of fly ash using the present laboratory method the optimum additives and the conditions might be evaluated. The right additive and conditions could then be used in an actual boiler in order to effectively reduce the deposit strength.

5.3.7 Sintering Characteristics of Several Fly Ashes in a Reducing Atmosphere

The sinter points of Upper Freeport fly ash shown in Figure

5.29 were 675°C in a reducing atmosphere and 800°C in air. This was in accord with the lower initial deformation temperature (IDT) in the reducing atmosphere (1205°C), rather than in air (1390°C). Figure 5.30(a) shows the compressive strength in air as compared to that in the reducing atmosphere as a function of temperature. The corresponding fractional (diameter)² change in pellet dimension with temperature is shown in Figure 5.30(b). The results of heating the Upper Freeport pellet in a reducing atmosphere indicated development of strength at lower temperatures ($800\text{--}1000^{\circ}\text{C}$), but with a lower maximum strength and smaller dimensional change at the elevated temperatures ($>1000^{\circ}\text{C}$). Figure 5.31 shows SEM photomicrographs of the cold Upper Freeport sintered pellets under the reducing atmosphere. The earlier development of sinter necks and the formation of glass at 950°C in the reducing atmosphere as compared with the pellet heat treated in air is clearly indicated.

All pellets heat treated in the reducing atmosphere were black, indicating that most of the iron was largely present in the reduced state. Figure 5.32 shows XRD patterns of the cold pellet where fayalite (Fe_2SiO_4), hercynite (FeAl_2O_4), quartz, mullite, magnetite, spinel ($\text{Fe,MgAl}_2\text{O}_4$), and traces of anorthite were identified. The iron in the reduced state could readily enter into aluminosilicate glass and form a lower melting point iron aluminosilicate glass. In addition, a low melting point fayalite crystalline phase formed from the reaction of FeO and silica. These newly formed low melting point phases could provide a liquid phase at lower temperatures than the glass material originally contained in the as-received fly ash. An anorthite phase was not seen in the pellets sintered in air, but a

Figure 5.29. Comparison of electrical sinter points of U. Freeport fly ash in air and in reducing atmosphere ($\circ$ in air; $\square$ in reducing atmosphere).

Figure 5.30. Comparison between (a) compressive strength and (b) the corresponding fractional change in (diameter)² as a function of temperature for U.Freeport fly ash sintered in air (○) and in reducing atmosphere (□).

Figure 5.31. SEM photomicrographs for the structure of cold pellets from U. Freeport fly ash, as a function of heat treatment temperature (for 1 hour) in reducing atmosphere; (a) 950 °C; (b) 1000 °C; (c) 1050 °C; and (d) 1100 °C.

Figure 5.32. X-ray diffraction patterns of U.Freeport fly ash sintered for 1 hour in reducing atmosphere; (a) as received fly ash; (b) at 950 °C; (c) 1050 °C; and (d) 1100 °C; only major peaks were labelled as Q = quartz, M = mullite, Y = fayalite, H = hercynite, F = magnetite, F* = hematite, and A = anorthite.

significant amount of anorthite appeared in the pellets sintered in the reducing atmosphere, presumably the presence of the greater liquid content under the reducing conditions facilitated the interaction of calcium ions with aluminosilicate glass to form anorthite. The quantity of crystalline phases of fayalite, hercynite and anorthite appeared to increase with temperature. This may account for the lower maximum strength and the reduction of strength at elevated temperatures ($>1000^{\circ}\text{C}$) as compared with the fly ash heat treated in air. The heat treatment of pellets in the reducing atmosphere was performed only up to 1100°C , since higher temperatures caused the pellets to deform.

It appears from these results that the mechanism of Upper Freeport fly ash sintering in both the oxidizing and the reducing atmospheres are the same except that iron in the reduced state forms new lower melting point phases causing the sintering to develop earlier than in air. To verify the effect of iron on the sintering of fly ash, fine powders ($-38\text{ }\mu\text{m}$) of hematite and magnetite were used as additives (30 wt%) by mixing with Upper Freeport fly ash before making a pellet. The sintering of fly ash with hematite and fly ash with magnetite were investigated both in air and in the reducing atmosphere. Addition of these two additives did not cause any change in the sinter point (800°C) of the original fly ash in air, but caused a reduction of the sinter point from 675°C to 600°C in the reducing atmosphere. Figure 5.33(a) shows the result of the effect of these additives on the compressive strength of the Upper Freeport fly ash as a function of temperature in air. As expected, both additives acted as an inert material which did not readily react with ash components

(a)

(b)

Figure 5.33. Compressive strength of U.Freeport fly ash (○), U.Freeport fly ash plus hematite (□), U.Freeport fly ash plus magnetite (◇), as a function of temperature (1 hour); (a) in air; (b) in reducing atmosphere.

under these conditions and, hence, resulted in a lower strength as compared with the original fly ash. SEM photomicrographs, as shown in Figure 5.34 show the typical morphological structure of the cold pellets with these additives heat treated in air. Phase analysis by XRD indicated that the hematite content remained unchanged, whereas the magnetite changed to hematite and remained constant throughout the range of investigated temperatures (see Figure 5.35 and Figure 5.36).

In the reducing atmosphere, the similar earlier development in strength was observed but with a lower maximum strength of the Upper Freeport fly ash with hematite and magnetite additives as compared to that of the original fly ash, as shown in Figure 5.33(b). SEM photomicrographs of the typical structure of the sintered pellets from the fly ash with these additives heat treated in the reducing atmosphere, showing glassy phase at lower temperatures ($900-950^{\circ}\text{C}$) and crystalline phases at higher temperatures ($1000-1025^{\circ}\text{C}$) are shown in Figure 5.37. Figures 5.38 and 5.39 give the XRD results from these sintered pellets which contained high amounts of fayalite and magnetite crystalline phase. These figures show that a large fraction of unreacted magnetite still remained in the sintered pellet. This excess of unreacted magnetite could act as an inert material in the sintered mass, because of its high melting point. The lower maximum strength of Upper Freeport fly ash as a result of the addition of these two additives could result from an extremely high solid crystalline content of the newly formed fayalite plus the unreacted excess amount of magnetite in the matrix. At temperatures greater than 1050°C , the pellets with these additives readily deformed.

Significant amounts of crystalline phases, probably fayalite,

Figure 5.34. SEM photomicrographs for the structure of the cold pellets from U.Freeport fly ash plus hematite sintered 1 hour in air at (a) 950 °C; (b) 1050°C; (c) 1100 °C; and (d) 1200 °C.

Figure 5.35. X-ray diffraction patterns of U.Freeport fly ash plus hematite sintered 1 hour in air at (a) 950 °C; (b) 1050 °C; and (c) 1150 °C; only major peaks were labelled as Q = quartz, M =mullite, F = hematite.

Figure 5.36. X-ray diffraction patterns of U.Freeport fly ash plus magnetite sintered 1 hour in air at (a) 950 °C; (b) 1050 °C; and (c) 1200 °C; only major peaks were labelled as Q = quartz, M = mullite, F = hematite, and B = magnetite.

Figure 5.37. SEM photomicrographs for the structure of cold pellets from U.Freeport fly ash plus hematite sintered 1 hour in reducing atmosphere at (a) 900 °C; (b) 950 °C; (c) 1000 °C; and (d) 1025 °C.

Figure 5.38. X-ray diffraction patterns of U. Freeport fly ash plus hematite sintered 1 hour in reducing atmosphere at (a) 850 °C; (b) 900 °C; and (c) 1000 °C; only major peaks were labelled as Q = quartz, M = mullite, F = magnetite, Y = fayalite, H = hercynite, and A = anorthite.

Figure 5.39. X-ray diffraction patterns of U.Freeport fly ash plus magnetite sintered 1 hour in reducing atmosphere at (a) 850 °C; (b) 900 °C; and (c) 1000 °C; only major peaks were labelled as Q= quartz, M = mullite, F = magnetite, Y = fayalite, H = hercynite, and A = anorthite.

also appeared in the cold sintered pellets from the high iron-Illinois #6 fly ash in the reducing atmosphere (see Figure 5.41). The major XRD crystalline phases of these pellets are shown in Figure 5.42. They were fayalite, hercynite, and anorthite. Figure 5.40 shows the strength as a function of temperature of this fly ash in the reducing atmosphere and in air. In the reducing atmosphere a greater strength was noted at the low temperatures, but at the higher temperatures (1100°C) the pellet readily deformed, as compared to that in air.

Gasifier fly ash produced from Illinois #6 coal under gasification conditions was also investigated. The gasification conditions were achieved in a 7 kg/h combustor by decreasing the flow of secondary air and admitting steam (Kinneman, 1983). The product gas was strongly reducing as indicated by the presence of high concentrations of carbon monoxide and hydrogen. The gasification condition retards the oxidation of iron compounds, thus the iron in the gasifier fly ash would probably largely exist in the reduced state. Figure 5.40(a) shows that the gasifier fly ash exhibited a higher maximum strength as compared with normal fly ash in air. Although iron in the reduced state could readily react with glass components to form a liquid phase at low temperatures in the reducing atmosphere, it also facilitated the formation of crystalline phases. This caused a reduction in strength and in deformation of the pellet at lower temperatures as compared with the normal fly ash (see Figure 5.40(b)).

Both gasifier and normal fly ashes which contained the same content of iron (see Table 5.3, page 219) were produced from the same coal. The dissimilarity in sintering behavior may have been the result

Figure 5.40. Comparison of sintered strength of Illinois #6 fly ash (○) and Illinois #6 gasifier fly ash (□); (a) heat treated for 1 hour in air; and (b) heat treated for 1 hour in reducing atmosphere.

Figure 5.41. SEM photomicrographs for the structure of the cold pellets from Illinois #6 fly ash, as a function of heat treatment temperature for 1 hour in reducing atmosphere; (a) 950 $^{\circ}\text{C}$; (b) 1000 $^{\circ}\text{C}$; (b) 1050 $^{\circ}\text{C}$; and (d) 1075 $^{\circ}\text{C}$.

of the difference in the form of the iron compounds in the two fly ashes. The iron in the reduced state may have provided great content of the low melting point iron glass in the gasifier fly ash, as compared to that of the normal fly ash. However, the normal fly ash and gasifier fly ash in both oxidizing and reducing atmospheres exhibited virtually no significant difference in phases identified in the XRD patterns, as shown in Figures 5.17, 5.42, 5.43 and 5.44.

Unlike the sintering behavior of Beulah fly ash in air which gave a small increase in strength with temperature, the sintering of Beulah fly ash in the reducing atmosphere exhibited a rise and fall of strength as a function of temperature. Figure 5.45(a) compares the compressive strength of this fly ash in both atmospheres. The pellet developed higher strength at lower temperature than in air (800 °C versus 900 °C) and had a higher maximum strength, which corresponded to the observed maximum shrinkage, as shown in Figure 5.45(b). The color of the pellets heat treated in the reducing atmosphere was black.

Figure 5.46 shows SEM photomicrographs of Beulah fly ash and their sintered products. The major XRD crystalline phases of these pellets are shown in Figure 5.47. Pellets heat treated at 850 °C in the reducing atmosphere forms kirchsteinite (CaFeSiO_4) and Ca-Fe olivines ($\text{Fe}_x\text{Ca}_y\text{SiO}_4$), along with the melilite phase described earlier. Kirchsteinite and Ca-Fe Olivines are crystalline phases known to form in blast furnace slag (Nurse and Midley, 1953, Allen and Snow, 1955, Sahama and Hytonen, 1957, and Deer et al., 1963). These crystalline phases formed from the reaction between fayalite and dicalcium silicate (Ca_2SiO_4) in the reducing environment (Bowen et al., 1933):

Figure 5.42. X-ray diffraction patterns of Illinois #6 fly ash sintered in reducing atmosphere for 1 hour; (a) as received fly ash; (b) 950 °C; and (c) 1025 °C; only major peaks were labelled as Q = quartz, M = mullite, S = CaSO_4 , F = hematite, B = magnetite, A = anorthite, Y = fayalite, and H = hercynite.

Figure 5.43. X-ray diffraction patterns of Illinois #6 gasifier fly ash sintered for 1 hour in air; (a) as received fly ash; (b) 1050 °C; and (c) 1150 °C; only major peaks were labelled as Q = quartz, S = CaSO_4 , F = hematite, M = mullite, and A = anorthite.

Figure 5.44. X-ray diffraction patterns of Illinois #6 gasifier fly ash sintered for 1 hour in reducing atmosphere; (a) as received fly ash; (b) 950 °C; and (c) 1025 °C; only major peaks were labelled as Q = quartz, A = anorthite, B = magnetite, Y = fayalite, and H = hercynite.

Figure 5.45. Sintering characteristic of Beulah fly ash sintered in air and reducing atmosphere; (a) compressive strength; and (b) the corresponding fractional change in (diameter)², as a function of temperature (1 hour heat treatment).

Figure 5.46. SEM photomicrographs of Beulah fly ash pellets heat treated in a reducing atmosphere for 1 hour; (a) 850 °C; (b) 950 °C; (c) 1000 °C; and (d) 1050 °C.

Figure 5.47. X-ray diffraction patterns of Beulah fly ash heat treated for 1 hour in reducing atmosphere; (a) as received fly ash; (b) 850 °C; (c) 1000 °C; and (d) 1050 °C; only major peaks were labelled as Q = quartz, S* = Na_2SO_4 , F* = hematite, P = spinel, MgFe_2O_4 , K = kirschsteinite, F = Ca-Fe Olivines, N = nepheline, G = gehlenite, and S = sodium melilite.

XRD analysis showed that the intensity of XRD peaks of kirchsteinite, Ca-Fe olivines and melilite phases increased with the heat treatment temperature in the reducing atmosphere. Iron compounds in the reduced state have a lower melting point and presumably would generate a substantial amount of liquid phase to contract particles in the pellets by surface tension forces, as shown in Figure 5.45(b). As a result, a high sintering rate, and hence, a high strength was observed in these pellets. At 1050^o C, a readily deformation and then expansion of the pellet started to occur which led to a reduction in the strength. The deformation could be the result of dissolution of some major crystalline phases. For example, nepheline ($\text{NaAlSi}_3\text{O}_8$) dissolves into the iron (in the reduced state) liquid phase as indicated in the equilibrium diagram of the system $\text{NaAlSi}_3\text{O}_8\text{-FeO-SiO}_2$ (Bowen and Schairer, 1938). The melting temperatures of some crystalline phases identified in this investigation are tabulated in Table 5.5.

The results from these tests suggest that the mechanism of the sintering of Beulah fly ash in the oxidizing and the reducing atmospheres are not the same. The sintering of Beulah fly ash in air appears to involve a viscous flow with a non-reactive liquid phase at low temperatures (<1150^o C), but exhibits a viscous flow with a reactive liquid phase at high temperatures (>1150^o C). In contrast, the sintering mechanism of Beulah fly ash in the reducing atmosphere is similar to the sintering of fly ashes from high-rank coals, that is, a viscous flow with a reactive liquid phase at low temperatures (<1025^o C) and a viscous flow with a non-reactive liquid phase at high temperatures (>1025^o C). The difference, however, has been in the

Table 5.5. Melting temperatures of some typical high temperature compounds in fly ash and sintered product as identified by X-ray diffraction analysis.*

Compound	Chemical formula	Melting point, °C
Akermanite	$2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	1458
Albite	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	1100
Anhydrite	CaSO_4	1450
Anorthite	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	1550
Corundum	Al_2O_3	2080
Cristobalite	SiO_2	1710
Fayalite	$2\text{FeO} \cdot \text{SiO}_2$	1205
Gehlenite	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	1590
Hauyne	$(\text{Na}, \text{Ca})_8 (\text{Al}_{12} \text{Si}_{12} \text{O}_{24}) (\text{SO}_4)_2$	800
Hematite	Fe_2O_3	1565
Hercynite	$\text{FeO} \cdot \text{Al}_2\text{O}_3$	1775
Kirchsteinite	CaFeSiO_4	1210
Lime	CaO	2570
Magnetite	Fe_3O_4	1590
Mullite	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	1810
Nephelene	NaAlSiO_4	1525 [@]
Nosean	$\text{Na}_8 \text{Al}_6 \text{Si}_6 \text{O}_{24} \text{SO}_4$	800
Periclase	MgO	2600
Quartz	SiO_2	1710
Sodium melillite	$\text{NaCaAlSi}_2\text{O}_7$	1080 [@]
Spinel	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	2135
Thenardite	Na_2SO_4	884
Tridymite	SiO_2	1710
Wustite	FeO	1370

@ decomposes

* Source = Goblirsch et al., 1983.

compounds formed in the sintered products: for example, kirchsteinite (CaFeSiO_4) was identified in the Beulah pellets heat treated in the reducing atmosphere, whereas fayalite (Fe_2SiO_4) was observed in the sintered products of fly ashes from high-rank coals.

5.3.8 Effects of Varying Chemical Composition Relevant to Fly Ash Sintering in Air and a Reducing Atmosphere

The size distribution, ash fusion temperatures, chemical and mineralogical composition of a mineral mixture to simulate Upper Freeport coal are tabulated in Tables 5.1-5.4 (see pages 228, 229, 230, 235 and 236, respectively). The ash fusion temperature of the mineral mixture agreed better with the high temperature ASTM ash than that of the fly ash produced from the same coal. This behavior reflects the close similarity in chemical composition of the mineral mixture and the ASTM ash. Figure 5.48 shows the sinter point of the mineral mixture. This material did not develop strength until its sinter point was reached (1025°C) in air. This temperature was 225°C above the usual sinter point of Upper Freeport fly ash. This difference is undoubtedly related to the difference in form of chemicals contained in the mineral mixture and the Upper Freeport fly ash. A higher temperature ($>1000^\circ\text{C}$) is required to produce a liquid phase during the sintering of the mineral mixture. The fly ash, on the other hand, already contains the glass phases necessary for initiating sintering at lower temperature ($>850^\circ\text{C}$). Figure 5.49 shows the strength plotted as a function of temperature. The corresponding fractional (diameter)² change in pellet dimension with temperature is also shown in Figure 5.49. The mineral mixture exhibited some

Figure 5.48. Sinter point determination for U.Freeport mineral mixture in air (○); U. Freeport mineral mixture in reducing atmosphere (△); Fused U.Freeport mineral mixture in air (●); U.Freeport fly ash in air (◇); and U.Freeport fly ash in reducing atmosphere (□).

Figure 5.49. Comparison of sintering behavior between U.Freeport mineral mixture in air (◇); U.Freeport mineral mixture in reducing atmosphere (△); Fused U.Freeport mineral mixture in air (□); and U.Freeport fly ash in air (○); (a) compressive strength; (b) fractional change in (diameter)² for U.Freeport mineral mixture in air and reducing atmosphere.

shrinkage, but no measurable strength when it was sintered at 1000°C in air. This shrinkage at the low temperature probably related to the thermal decomposition of some minerals resulting in a smaller pellet volume, but not due to sintering. The sintering behavior of the mineral mixture in air showed the same kind of rise and fall in strength with temperature as that of the fly ash. This information suggests that the mechanisms of sintering of both materials may be the same, except that the sintering of the mineral mixture occurs at a higher temperature ($>1025^{\circ}\text{C}$) since the sintering depends on the rate of glass phase formation which requires a higher temperature and longer time to produce sufficient amount of glass phase necessary for initiating and developing strength.

Figure 5.50 shows SEM photomicrographs of the cold pellets sintered in air. The formation of a glassy phase is clearly indicated in the pellet heat treated at higher temperatures ($>1050^{\circ}\text{C}$). The crystalline phases identified by XRD formed at 1050°C in air include quartz, hematite, mullite, corundum (Al_2O_3), spinel ($\text{MgFeAl}_2\text{O}_4$) and anorthite, as shown in Figure 5.51. These crystalline phases (except anorthite) are those which would be expected from individual thermal decomposition of the mineral phases. Anorthite could result from the reaction between calcium derived from the thermal decomposition of gypsum and clays. The intensities of XRD peaks of anorthite, corundum and mullite increased with temperature, whereas quartz gradually decreased, and the other crystalline phases were unchanged. Increase in the formation of these crystalline phases may account for the reduction of strength at elevated temperatures ($>1150^{\circ}\text{C}$).

To obtain a material of high uniformity and time-temperature

Figure 5.50 SEM photomicrographs for the structure of cold pellets from U.Freeport mineral mixture, as a function of heat treatment temperature for 1 hour in air; (a) as received material; (b) 1025 °C; (c) 1100 °C; and (d) 1200 °C.

Figure 5.51. X-ray diffraction patterns of U.Freeport mineral mixture heat treated for 1 hour in air; (a) 1050 °C; (b) 1100 °C; and (c) 1200 °C; only major peaks were labelled as Q = quartz, M = mullite, F = hematite, A* = corundum, P = spinel, A = anorthite.

history simulating a fly ash, a sample of mineral mixture shown in Table 5.4 was fused to a glass at 1750°C in a methane-oxygen flame. It was then cooled and hand pulverized to the size distribution shown in Table 5.1(b) (see page 229). The fused material gave a sinter point of 850°C in air which was 200°C lower than the unfused mineral mixture (see Figure 5.48). Figure 5.49 also shows the result of the sintered strength as a function of temperature for the fused mineral mixture. Unfortunately, it was not realized at first that the fused mineral mixture had a much coarser size than either the unfused mineral mixture or the Upper Freeport fly ash, and it is known that the particle size affects the sintering process. However, Figure 5.49 shows that the fused mineral mixture developed strength at 800°C which is 200°C lower than the unfused material. The fused mineral mixture of similar chemical composition to the mean fly ash behaved somewhat similar to the fly ash but with much lower maximum strength, as expected from its coarser size distribution.

Significant amounts of glassy phase and some crystalline phases similar to the Upper Freeport fly ash were identified in the XRD patterns of the fused material as shown in Figure 5.52. The rise and fall of strength with temperature suggests that the same sintering mechanism as the Upper Freeport fly ash applied also to the fused mineral mixture. The crystalline phases which increased in XRD peak intensities with temperature and were responsible for the reduction in strength at the high temperatures ($>1050^{\circ}\text{C}$) were identified as anorthite, corundum and mullite.

The addition of 30 wt% pyrite as a fine powder of the size distribution shown in Table 5.1(b) (see page 229) to the mineral

Figure 5.52. X-ray diffraction patterns of fused U. Freeport mineral mixture heat treated for 1 hour in air; (a) as prepared; (b) 950 °C; (c) 1050 °C; and (d) 1150 °C; only major peaks were labelled as Q = quartz, M = mullite, F = hematite, A = anorthite, B = corundum, and C = cristobalite.

mixture simulating Upper Freeport coal gave essentially no effect on the development of strength under the conditions used in this study. The iron oxide produced by the relatively slow heating rate was apparently not readily reacted in the sintering mass. However, addition of pre-formed iron silicate and sodium silicate (for preparation see page 271) had very significant effects on the sintering of the mineral mixture, as shown in Figure 5.53. This figure reports a reduction in the sinter point of the mineral mixture to 600°C when sodium silicate was added and to 850°C when iron silicate was added. These additives caused immediate development of strength above 800°C , more rapidly with the combination of sodium-iron silicate. Comparison with the results from Upper Freeport fly ash and the fused mineral mixture show the same kind of rise and fall of strength with temperature, suggesting that some phases of the fly ash and the fused material is in the form of low melting point silicate glass, perhaps both alkali and iron silicate composition.

To test the possible effect of alkali in the sinter, pellets of the mineral mixture were prepared containing 5 wt% Na_2O (-10 micrometers) formed by heating sodium carbonate. Since Na_2O is infusible, any increase in strength at low temperatures must result from the reaction of Na_2O with some components of the mineral mixture. The sinter point of this material with the Na_2O additive was 850°C and the result of its effect on sintered strength as a function of temperature is shown in Figure 5.53. Although the strength started to develop at lower temperatures ($<1050^{\circ}\text{C}$), the maximum of strength was lower than the mineral mixture without the Na_2O additive.

Figure 5.54 shows XRD patterns of the cold sintered products

Figure 5.53. Effect of additives to the U.Freeport mineral

mixture:

- U.Freeport mineral mixture (S.P. 1025 °C);
- U.Freeport mineral mixture + 10% sodium silicate (S.P. 600 °C);
- △ U.Freeport mineral mixture + 10% iron silicate (S.P. 850 °C);
- ◇ U.Freeport mineral mixture + 5% sodium silicate + 5% iron silicate (S.P. 600 °C);
- U.Freeport mineral mixture coated with Na_2CO_3 (3%) (S.P. 700 °C);
- ▲ U.Freeport mineral mixture coated with Na_2CO_3 (9%) (S.P. 700 °C);
- ◆ U.Freeport mineral mixture + 5% Na_2O (S.P. 850 °C);
- U.Freeport mineral mixture + 20% Na_2O (S.P. 850 °C).

Figure 5.54. X-ray diffraction patterns of U.Freeport mineral mixture + Na_2O addition heat treated for 1 hour in air; (a) 950 °C; (b) 1000 °C; and (c) 1100 °C; only major peaks were labelled as Q = quartz, M = mullite, A = albite, and F = hematite.

from the mineral mixture with Na_2O additive. The phases analyzed by XRD which are associated with the development of strength at 950°C include glass, quartz, hematite, mullite and anorthite. Formation of the glassy phase, probably a sodium silicate, could originate from a low melting eutectic mixture of $\text{Na}_2\text{O}-\text{SiO}_2$ at 800°C (Kingery et al., 1976). The formation of a low melting point of sodium silicate glass initiated sintering and the strength developed earlier at temperatures as low as 850°C . The lower maximum strength observed in this system as compared with that of the mineral mixture without an additive could result from rapid formation of anorthite crystals which removed the bonding sodium silicate glass. Too high an addition of Na_2O (20 wt%) led to even lower strength, suggesting that the properties of crystalline anorthite become the determining factor in the sintering process. The pellet also deformed at low temperatures (1100°C). Addition of Na_2O to the fused synthetic ash gave little effect. This suggests that the effect of alkali is via reaction with certain fly ash spheres of different composition than the mean.

To give a more intimate contact of alkali with the particle surfaces the mineral mixture were coated by impregnation with a sodium carbonate solution followed by drying. The results are also shown in Figure 5.53. XRD patterns shown in Figure 5.55 gave the phases which include glass, the sodalites-type minerals (nosean and hauyne), anorthite, hematite and quartz. The glass phase and the sodalites (melting point 800°C) provided substantial amounts of liquid phase to the system and made sintering start immediately at 850°C to a high strength. At higher temperatures ($>1050^\circ\text{C}$) XRD intensity peaks of quartz gradually disappeared, whereas that of sodalites increased in

Figure 5.55. X-ray diffraction patterns of Upper Freeport mineral mixture + Na_2CO_3 (coated on particles) heat treated for 1 hour in air; (a) 900°C; (b) 1000°C; (c) 1050°C; and (d) 1100°C; only major peaks were labelled as Q = quartz, N = nosean, H = hercynite, F = hematite, and A = albite.

intensity. The absence of mullite peaks on the XRD patterns even at high temperatures (1100°C), suggests that most of the clays were transformed to glass and crystalline phases of sodalites rather than mullite. The pellets deformed immediately after 1100°C , and at even lower temperatures (1050°C) with the higher concentration of sodium carbonate coating. The addition of surface-coated sodium carbonate to the fused mineral mixture had little effect, showing that the fused material already contained the glass components necessary for bonding.

The sinter point of the mineral mixture and the Upper Freeport fly ash under the reducing atmosphere were similar, as shown in Figure 5.48. This is in contrast with the observations in air where the materials exhibited a 200°C difference in their sinter points. Figure 5.49 shows the strength of mineral mixture sintered in the reducing atmosphere plotted as a function of temperature. The pellets developed high strength at lower temperatures than in air ($>850^{\circ}\text{C}$ versus $>1000^{\circ}\text{C}$), but still showed the same kind of rise and fall of strength with temperature as in air. SEM photomicrographs of the cold pellets sintered at 900°C to 1000°C showed glassy phase formation (see Figures 5.56(a) and 5.56(b)). The phase analysis using XRD, as shown in Figure 5.57, gave glass, quartz, corundum, magnetite, fayalite and anorthite. The glass formed at this low temperature (800°C) could be the result of iron in the reduced state penetrating into the thermally decomposed clays to produce a low melting point iron aluminosilicate glass. The iron in the reduced state, probably FeO , also reacted with quartz to form fayalite. The reduction in strength after 1025°C appears to be associated with the increasing formation of anorthite and fayalite crystals with temperature. The crystals are clearly

Figure 5.56. SEM photomicrographs for the structure of cold pellets from U.Freeport mineral mixture heat treated for 1 hour in reducing atmosphere; (a) 900°C; (b) 1000°C; (c) 1050°C; and (d) 1100°C.

Figure 5.57. X-ray diffraction patterns of U.Freeport mineral mixture heat treated for 1 hour in reducing atmosphere; (a) 850 °C; (b) 950 °C; and (c) 1100 °C; only major peaks were labelled as Q = quartz, Fa = fayalite, A = anorthite, F = magnetite, and Fe = iron (0)?

indicated in Figure 5.56(c). The pellet deformed readily at 1100°C.

It has been observed that iron gives no significant effect on the development of strength in air but is responsible for the earlier development of strength in the reducing atmosphere. To verify this fact, pyrite was omitted from the mineral mixture and the mineral mixture without pyrite was tested under a reducing atmosphere. Figure 5.58 shows the comparison between the development of strength plotted as a function of temperature for the mineral mixture containing pyrite and the same mineral mixture without pyrite in the reducing atmosphere. The earlier development and higher strength of the mineral mixture containing pyrite were observed as compared to that of the mineral mixture without pyrite. This observation emphasizes the influence of the reducing atmosphere on the sintering behavior when iron is present. Subsequently, iron in the reduced state reacts with other components to produce a low melting point glass phase that helps to facilitate sintering at lower temperatures as compared to air.

5.4 Summary

The results of sintering tests are summarized in the following points:

(1) The Barnhart and Williams's compressive strength test appeared to be a reliable and reproducible method for the fundamental studies of the characteristics and mechanisms of fly ash sintering. This test permitted interpretation and evaluation in terms of the physical and chemical changes of the sintered ash particles as related to deposit formation process.

(2) Sintering parameters such as time and temperature could be

Figure 5.58. Compressive strength as a function of temperature of U.Freeport mineral mixture containing pyrite (Δ) and U.Freeport mineral mixture without pyrite ($\circ$) heat treated for 1 hour in reducing atmosphere.

used to follow the progress of deposit strength, with temperature having the greater effect. The test results indicate that increased temperature is the fastest and the most direct manner to cause sintering to occur.

(3) The compressive strength of fly ash sinters as a function of temperature is an important descriptor of the deposit forming propensity of the coal, as shown by:

- The lower maximum strength of the Montour fly ash than that of the Upper Freeport fly ash appears to be in accord with the utility experience using these two coals, since Montour coal gives less problems with upper furnace sootblowing operation than Upper Freeport coal.

- The lower strength of Beulah fly ash from Beulah lignite as compared to that of fly ash from high-rank coal corresponds to the general observation that low-rank coals give less slagging problems (as distinct from fouling problems) than do the high-rank coals.

(4) The sintering behavior of fly ash from high-rank coal showed a characteristic of a rise and fall in strength with temperature. This character reflects the changing in both physical and chemical nature of the bonding phase, and hence the changing of the sintering mechanism with temperature, as shown by:

- In the lower temperature range (850°C - 1050°C), there was an increase in the amount of the liquid bonding phase and the rate of dissolution of the solid phase into the liquid, resulting in a rapid sintering rate and a large increase in strength with temperature.

- In the higher temperature range (1050°C - 1200°C), there were phase decomposition and chemical reactions that accompany or

precede the sintering process. These removed some of liquid bonding phase and produced solid crystalline phases. The crystalline phases did not readily dissolve into the liquid and their amounts increased with temperature, resulting in a rise of the viscosity of the residual liquid and a reduction in the rate of sintering and strength.

Thus, there probably exists two viscous flow mechanisms involved in the sintering of fly ashes from high-rank coals, one with a reactive liquid phase at the lower temperatures (850-1050^o C) and one with a non-reactive liquid phase at the higher temperatures (1050-1200^o C).

(5) The sintering behavior of the fly ash from the Beulah low-rank coal showed a small increase in strength and exhibited no shrinkage with temperature and time. At the higher temperatures (>1150^o C), however, there was a considerable strength and shrinkage with temperature and time. This behavior indicated that different mechanisms exist between the sintering at the lower temperatures and that at the higher temperatures, as shown by:

. In the low temperature range (900^o C-1150^o C) there was devitrification to change some of the glass material in the fly ash into crystalline phases, resulting in a slow increase in strength with temperature.

. At the higher temperatures (>1150^o C), there appears to be a substantial amount of liquid bonding phase formed and its amount increased with temperature, resulting in a greater increase in strength with temperature.

Thus, there probably exists two viscous flow mechanisms involved in the sintering of fly ash from Beulah lignite, one with a

non-reactive liquid phase at the lower temperatures (850-1150^o C) and one with a reactive liquid phase at the higher temperatures (>1150^o C).

(6) The glass materials contained in the as-received fly ashes from high-rank coals were components that contribute most to the formation of strong deposits. The glass materials in fly ash formed a liquid phase at the higher temperatures. Solidification of the liquid phase as glass on cooling served as an excellent bonding phase and the associated extensive sintering provided high strength to the matrix.

(7) In contrast, most of the glass materials associated with the high concentration of sodium and calcium species contained in the as-received fly ash from low-rank Beulah coal underwent devitrification to form crystalline phases during sintering. The interlocking of crystal bridges and the associated sintering provided a considerable strength to the matrix but still much lower than the strength of the fly ash from high-rank coal containing bonding glass.

(8) It follows, therefore, that the greater amount of glass materials contained in the as-received fly ash may give a greater slagging tendency and a greater deposit removal problem. However, the properties of the glass materials and the type and amount of the associated calcium and sodium species contained in the fly ash are a more critical factor than the amount of the glass material alone. The most important point is that they are related to the difference in the sintering characteristics and mechanisms between the fly ashes from high-rank and low-rank coals.

(9) The sintering of fly ash occurs mostly at the surfaces of the fly ash particles as shown by:

.Lack of the glass material at the surfaces of the HF-washed fly ash particles produced a very weak deposit.

.Coating of sodium species at the surfaces of the synthetic mineral mixture particles produced a stronger deposit at lower temperatures than those added as a pulverized form into the bulk mass.

(10) The addition of calcium and sodium species into the Upper Freeport fly ash enhanced the sintering rate at the lower temperatures ($<1000^{\circ}\text{C}$) by the formation of a low melting point glassy phase via a reaction with certain fly ash spheres of different composition than the mean. At the higher temperatures ($>1000^{\circ}\text{C}$), however, higher concentration of these species devitrified the liquid bonding phase to form crystalline phases resulting in a weak deposit.

(11) Calcium in an appropriate amount is a good network modifier which is capable of breaking up the glassy network and thus leading to crystallization (devitrification). Calcium compound thus is a good additive to reduce the strength of deposit. However, the calcium additive is effective only at high temperatures that enable devitrification to occur, that is $>1000^{\circ}\text{C}$.

(12) Sodium and iron in a closed association with the glass material in fly ash may lead to a greater slagging tendency and a greater deposit removal problem. The probable explanation to described the role of iron and sodium in the sintering of fly ash that they may form low melting point glasses that contribute most to rapid sintering of fly ash. The important point is that they do not readily devitrify the associated glasses to form crystalline phases as compared to calcium. Therefore, they do not significantly reduce the amount of the bonding

liquid phase, at least under the conditions used in the present study.

(13) Iron is responsible for initiating and enhancing the sintering rate at lower temperatures in the reducing atmosphere as compared to those in air. The iron in the reduced state readily enters into the glassy network to form a lower melting point iron glass enabling sintering to take place.

(14) Chemical reactions and phase decomposition during the sintering of fly ash in the reducing atmosphere produce mainly low melting point compounds (e.g., fayalite and kirschsteinite), whereas, the high melting point compounds (e.g., mullite and anorthite) occur in the sintering of fly ash in air. As a result, the deformation of the fly ash pellet in the reducing atmosphere occurs at lower temperatures than in air. This fact also yields an insight into the observation that the ash fusion temperature in the reducing atmosphere is generally lower than in air.

(15) The time-temperature history has a pronounced effect on the sintering behavior of a given fly ash. This phenomenon was observed when evaluating the fused and the unfused mineral mixture, with the fused material exhibiting lower sinter point and developing higher strengths at lower temperatures than the unfused material (800°C versus 1000°C).

(16) The mineral mixture initially forms a glass phase from thermal decomposition and chemical reaction between the mineral components and subsequently develops strength by viscous flow sintering. The sintering mechanism is quite similar to that of the fly ash, except that the sintering of the mineral mixture occurs at higher temperatures ($>1000^{\circ}\text{C}$).

(17) The mixture of soda glass and alumina mixture is a good model system to illustrate a glassy phase formation and displays a viscous flow mechanism. The system, however, does not perfectly simulate the complex system of fly ash sintering that involves chemical reactions.

(18) The results of sinter point determination using the ash electrical resistance method indicates that this method demonstrates the onset of sintering due to the presence of a liquid phase from the lowest melting point component in fly ash, but not due to the increase in sinter necks. A fly ash with a low sinter point which indicates earlier sintering does not necessarily produce a strong deposit. This is true when there are chemical reactions to remove the bonding phase necessary for the sintering process the resulting deposit may be brittle and easy to remove by the sootblower operation.

Chapter 6

CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

6.1 Conclusions

The objective of this study was to gain a better understanding of the mechanisms of the initiation, growth and sintering processes involved in slag deposit formation in utility boilers. Three laboratory tests were carried out to investigate these processes which were the sticking test, the vertical externally-heated tube furnace test, and the sintering test. Although it has not been proven that the vertical externally-heated tube furnace test is a correct simulation of combustion and deposition in a utility boiler, yet the results are sufficiently informative to be used in deducing a preliminary hypothesis for the formation of deposit in this type of laboratory furnace. The results from the sticking test and the sintering test were included to support the proposed hypothesis.

The model for deposition is as follows. The fly ash and the flue gas stream accelerate as they pass through the constrictor, and undergo a sharp change in direction as they encounter the substrate. This creates a higher gas velocity in the direction of the incoming hot gases toward the center of the substrate as compared to that which flows around the substrate. The average size of ash particles in the deposit mass was large as compared to that of the dust material deposited around the deposit mass. This indicates that the ash particles adhere and form a deposit mass probably by an inertial impaction mechanism, whereas the smaller dust particles tend to follow a streamline of the flue gases and deposit probably by a particle-

diffusion mechanism (Brownian and/or thermophoresis).

The deposit forming at the center of the substrate has, therefore, the typical physical appearance of a cone or a mountain that grows toward the direction of the incoming hot gases. The mechanism of growth is mainly by the direct head-on impingement as indicated by the growth lines in the deposit. It may be hypothesized that the formation of a deposit mass is assisted by:

- . Larger and molten fly ash particles;
- . Higher gas velocity;
- . Higher gas temperature;
- . Direct head-on impingement.

Preliminary results showed that a weaker deposit was formed under a lower gas velocity condition. This shows that gas velocity has a significant influence upon the amount, growth and properties of deposit. Systematic experiments to test the other variables involved in the deposit formation remain an objective for future work.

Most of the high-rank coals (bituminous) tested in this furnace exhibited an accelerated rate of growth, whereas most of the low-rank coals (subbituminous and lignites) showed a more uniform rate of deposition. The variation of sticking coefficients with time are distinctive for each coal. Under the same testing conditions in this laboratory furnace, it may also be hypothesized that different coals have different sticking coefficients because of the following possibilities:

- . The proportion of fly ash particles which are molten or solid but sticky are different for different coals;
- . The size distribution and density of fly ash particles

produced from different coals are different;

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

It has been recognized that the physical and chemical properties of a deposit, such as mechanical strength and resistance to thermal shock, are greatly influenced by the microstructure of the deposit. It is now possible to explain and postulate hypotheses about the microstructure of the deposit formed in this laboratory furnace.

The initiation of deposit 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 hemispherical particles form and this creates more roughness to the surface for further deposition. The fraction of ash droplets that form the initial layer of the deposit from high-rank coals was rich in Fe and that for the deposit from low-rank coals was rich in both Fe and Ca.

It was found that upon shear the oxide layer was broken off the substrate, indicating that the adherence between the oxide layer and the initial layer of deposit was stronger than the adherence of oxide layer to the metal. 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. In addition, it seems likely that a layer of iron oxide on the substrate probably reduced

the rate of heat conduction away from the interface and kept the ash drop less viscous for a longer time, allowing more chemical compatibility at the interface.

Synthetic coal containing pyrite grew a strong deposit and formed a strong initial layer due to a low viscosity of pyrrhotite (formed from thermal decomposition of pyrite), which gave a low apparent contact angle and a good chemical compatibility with the relatively cool substrate. Synthetic coal containing illite, on the other hand, grew a strong deposit but did not involve a strong initiation layer, indicating that the glass formed from illite was highly viscous, which gave a high apparent contact angle with the substrate, thus not leading to a strongly bonded initial layer. The very weak adhesion of the 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 microporosity of the steel surface. From this information it is possible that the hypothesis postulated from the previous sticking studies (Moza, Abbott, and Austin, 1982) may also be applied here, that is, the adhesion force depends on such factors as viscosity and chemistry of the ash drops and the physical and chemical properties of the substrate surface.

Following the initial layer of deposit, ash accumulation to form a massive deposit depends on particle to particle adherence as the deposit grows. Although some of the incoming fly ash particles impact onto the particles of the initial layer of deposit, it is possible that a large fraction of the fly ash particles are simply trapped by the rough surface created by the initial layer. As the

deposition proceeds, this lower portion of deposit is eventually buried underneath a sintered deposit mass which forms as it builds up from the hotter surface of the upper layers of deposit. The lower portion of deposit is insulated by the upper layers of the growing deposit, and subsequently exists as a loose and slightly sintered layers due to the low temperatures in this region.

The growth mechanism following the lower portion of deposit is quite obvious, since the deposit grows toward the incoming hot gases, the mass becomes hotter as it builds up and collisions of fly ash with a sticky deposit are more likely to result in sticking. When the deposit reaches a certain height, the top of the deposit may give virtually complete capture of the fly ash (sticking coefficient = 1). However, as the deposit grows toward the constrictor, the changing of deposit shape alters the flow of gas around the deposit. Consequently, there appears to be a fraction of fly ash entering the constrictor that simply passes over the deposit.

The role of alkali and sulfur species in the formation of deposits cannot be deduced from the present study, since the furnace configuration and operating conditions had relatively short cooling time for the flue gas before impacting on the test probe, therefore the vaporized alkali and sulfur may not nucleate and condense on the deposit mass. However, the condensation of sodium sulfate as crystals found on the relatively cool surface outside the deposit mass region probably indicates a vapor phase deposition mechanism. Deposits formed from synthetic coal containing minerals but no alkali, showing that the presence of volatile or condensed alkali species is not necessary for deposit formation in the present study.

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 deposit, and hence a deposit has a microstructure leading from the slight sintering of the lower layers, to the stronger sintering of the upper layers, and to the strongly melted top. The lower layers of deposits from high-rank 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 deposit from high-rank coals, whereas a higher amount of crystalline phase occurred at the top of deposit from low-rank coals.

Results from the sintering investigation of fly ash from high-rank coal indicate that viscous flow sintering is promoted by a glass material in the spherical fly ash particles, resulting in a large increase in strength with temperature and a higher amount of bonding glassy phase whereby the shape of the initial spherical fly ash particles is no longer distinguishable. This is essentially similar to the sintering occurring at the high temperature regions (800-1200°C) of the deposit from high-rank coals. Results from the sintering test using fly ash from low-rank coal, on the other hand, exhibit a small increase in strength with temperature due to the chemical reaction which transforms the glass material in the fly ash into the crystalline phase. This is not surprising, since the bulk composition of the fly ash suggests that many crystalline phases such as gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) as predicted by the phase diagram are likely to occur at the sintering temperature as

well as at the high temperature regions of the deposit.

The relative amounts of glass and crystalline phases formed during sintering is a critical parameters affecting the strength of deposit. This was observed from the sintering test where a reduction in strength of fly ash from high-rank coal heat treated at high temperatures ($>1050^{\circ}\text{C}$, 1 hour) was found to be associated with the crystalline phase formed during sintering. The formation of crystals raises the viscosity of the residual liquid and hence, retard the rate of sintering process. Compounds added to promote the crystallization of the glass material in the fly ash from high-rank coal reduce the strength of sintered product. In addition, sintering of fly ash from high-rank coal after the removal of the glass material also gives a weaker sintered product.

Since glass material in fly ash 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 high-rank coal in the reducing atmosphere which developed a higher strength at a lower temperature than in air: this is probably due to the iron the reduced form (Fe^{+2} and Fe^0) entering into the glassy network of fly ash component to form a lower melting point iron glass phase enabling sintering to take place. Synthetic coal containing illite that formed a very strong sintered deposit, is another example to illustrate the importance of a low melting point glass which promotes viscous flow sintering process at a relatively low temperature.

6.2 Suggestions for Future Research

The present sticking test has two deficiencies. The temperature of the molten ash drop at the point when it releases from the platinum wire should be controlled to be the same for every ash or mineral composite. This problem can be overcome by the following method for retaining the ash drop until the desired temperature of the molten drop is reached. Preliminary tests showed that an ash drop would not fall if a thicker platinum wire (0.4 mm in diameter) was used to hold the ash drop. The thicker wire provided a greater surface area and tension for the ash drop to remain suspended on the wire. The ash drop and the wire can then both be dropped onto the steel substrate when the desired temperature of the molten drop is reached. For the material that has a very low surface tension and viscosity, such as pyrite and some fly ashes from low-rank coals, even the thicker wire may not retain the droplet for a sufficient time to reach the desired temperature. In this case, melting the pellet by the horizontal way and subsequently releasing the droplet by the vertical way can be very helpful because the surface tension of the droplet acts on the larger effective surface area of the wire in the horizontal way and thus can retain the droplet at a longer time as compared to that in the vertical way. An optical pyrometer or a thermocouple embedded in the ash pellet can be used to measure the temperature of the droplet as a function of time; then fixing the time of melting of the ash pellet in the flame determines the drop temperature. Since each ash or mineral composite may not exhibit the same time for the ash drop to reach the desired temperature, the melting time should be determined before performing the sticking test. In addition, the method of

measuring the adhesion strength between the ash drop and the steel substrate should be improved. A miniature penetrometer device for shearing off the ash drop from the horizontal substrate will give a better accurate determination of adhesive strength than the present shearing method involving tipping the substrate and furnace.

The research work that may be pursued using the sticking apparatus includes (1) repeating some of the previous tests, particularly those performed to investigate the effects of variation in chemical composition of the minerals and coal ashes from high- and low-rank coals; (2) testing fly ash collected from the vertical externally-heated tube furnace, as compared to coal ash from the high temperature ASTM and the low temperature ashing techniques, to develop a more representative ash system for evaluating sticking behavior; (3) performing tests to correlate the results from sticking behavior determined in the sticking apparatus to the actual sticking behavior of ash in the vertical externally-heated tube furnace; and (4) further testing of prospective materials with low slag adhesion properties for use as furnace wall tubes and heat exchanger tubes in utility boilers and gasifiers.

Several improvements should be performed before continuing the research using the vertical externally-heated tube furnace. A new pulverized coal feeding system is required to feed the whole size of pulverized coal. The development of a microstrength tester for strength probing of the deposit is essential since the strength of deposit is as important as the rate of growth of the deposit. The furnace used in the present study has a relatively short time of cooling of the fly ash and the flue gas before impacting on the test

probe and hence the furnace conditions closely simulate the slagging of boiler deposits on the furnace walls. In order to simulate the upperwall slagging and fouling in the convective regions in the utility boiler, another furnace for extension of the present furnace will be necessary to give a longer time of cooling of the fly ash and the flue gas before impaction on the test probe. Examination of chemical composition of deposited particles using qualitative SEM-EDS should be replaced by quantitative SEM-EDS analysis. This approach may be a useful way to measure chemical compositions of the ash from the initial layer to the last surface of deposit. In addition, quantitative analysis of studies of suites of fly ash particles will enable comparisons between the ash in the deposit and the total fly ash collected from the same furnace without deposition.

The fact that the temperature at deposit surface affects the deposition mechanism and it relates also to the extent of sintering and chemical reaction that occur following deposition. Therefore the temperature differentiation at the surface of deposit layer with each successive layer growing upon it, is the important information necessary for a better understanding of the mechanism of deposit formation. Determination of the temperature profile in the deposit during deposition may be accomplished by growing deposit on a thermocouple that is situated at a certain height from the substrate.

The small scale of the vertical externally-heated tube furnace enables closely controlled tests to be performed with small quantities of material, thus there are several investigations that can be conducted. These include a systematic study of the variables involved in addition to coal type and mineralogy, that is, flame temperature,

gas temperature and velocity in the region of deposition, substrate temperature and substrate surface treatment, etc. These parameters affect the type of deposition processes, and the amount and properties of resultant deposits. It is also possible to use this furnace on various cleaned fraction of coals, on acid-washed ion-exchanged coals, micronized coals, etc. The synthetic coals used in the present study yielded too high volatile matter to simulate the actual coal and therefore, its formulation should be improved. Graphite powder may be incorporated into the polymer in order to increase the burn-out time. It will then be possible to study the effects of the size of mineral additions as well as the types of minerals.

The aspect requiring the most attention in the future work using the vertical externally-heated tube furnace is to compare the ash deposition behavior exhibited in this furnace with the pilot-scale furnace and full-scale test experience of other workers with the same coals, etc.

Future work using the sintering test should include the study of several fly ashes from low-rank coals having a wide range of chemical compositions. However, the investigation should be performed in an atmosphere that closely simulates the sintering of fouling deposits on the convective heat transfer surfaces. Another furnace equipped with a continuous feeding system will be necessary for producing a flue gas composition containing alkali and sulfur vapors for introduction into the present sintering furnace. Future work should also include a definitive experiment to study the chemical processes acting in the formation of the melilites and the sodalites crystalline phases in deposits from low-rank coals. These crystalline

phases are thought to have significant roles in development of sintered strength in deposits from low-rank coals. These tests can be performed using mineral mixtures of known compositions to match the mineral composition of a typical low-rank coal. This requires the mineral mixture to be passed through a time-temperature history, and to have particle shape and size distribution, comparable to the fly ash from utility boilers. The vertical externally-heated tube furnace can be used to produce these synthetic fly ashes. Identification and quantification of the glass and the crystalline phases in the sintered products from this mineral mixture and the actual fly ash are necessary in order to give correlations with strength.

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