oxides in the ash (ref. 30). The exact manner in which sulfates form is not well understood. It has been postulated that sulfates form in the gas stream and condense on the surfaces of materials such as fly ash particles or boiler surfaces. However, it is more likely that sulfates are formed on particle or deposit surfaces where an alkali layer (e.g. NaOH) is first deposited, followed by the sulfur oxide interaction.

The behavior of alkali species such as sodium is extremely important with respect to the formation of convective pass fouling deposits. The mechanisms by which sodium forms deposits have been investigated by a number of researchers (refs. 23, 31). Sodium present as salts of organic acid groups in the coal will readily volatilize in a pulverized coal flame. According to Raask (ref. 6), volatile sodium can easily dissolve in the surfaces of silicate particles or become sulfated. Sodium silicate ($Na_2Si_2O_5$) was found to be thermodynamically more stable than sulfates at temperatures from 1470 - 1870 K, while sodium sulfate was stable below approximately 1370 K. In fact, the formation of Na_2SO_4 at temperatures less than approximately 1300 K inhibited the formation of sodium silicate (ref. 32). Therefore, the distribution of volatile sodium between silicate components of the ash and sulfate is influenced by temperature, as well as the residence time, of the particle in the flame. In addition, the association of the silicate mineral grains within the Na-rich organic portion of the coal will allow for the reaction of sodium to form low melting point sodium-silicates. This will limit the vaporization of the sodium during combustion. Raask suggests that, on the average, 60% of the sodium is dissolved in the silicate phase and the remaining percentage will form sodium sulfate (ref. 6). This estimate appears to be quite high for western U.S. coals having high sodium contents, but may be reasonable for coals having lower sodium contents and higher concentrations of silicate minerals.

Wibberley and Wall (ref. 33) examined the reactions involving silicon-bearing minerals and volatile sodium. Quartz subjected to high temperature gases in a vertical tube furnace was found to be relatively unaltered in the furnace. However, in the presence of alkali in the furnace gases, a low-viscosity sodium silicate phase was formed. Experiments were also performed to simulate deposit formation, using both quartz and a mixture of quartz and NaCl. The results indicated that the formation of a low-viscosity sodium silicate layer in the presence of NaCl was responsible for deposit formation. No deposit formed when using quartz alone.

Vapor pressure measurements and thermodynamic calculations (ref. 34) suggest that vapor phase sodium and potassium hydroxides or chlorides are only present in significant quantities above approximately 1200 K. Below 1200 K, the alkalies are present mainly as condensed sulfates. In addition, reactions of alkali sulfates with aluminosilicates

are thermodynamically favored over reactions with silica or quartz, and the reaction with aluminosilicates should proceed above approximately 1000 K.

4.4 DEPOSIT INITIATION

4.4.1 Ash Intermediate Species Transport

The transport of intermediate ash species is a function of the state and size of the species and system conditions such as gas flow patterns, gas velocity, and temperature. Several processes are involved as described by Raask (ref. 6) and Rosner *et al.* (ref. 35).

The primary transport mechanisms are illustrated in Fig. 4.8. The small particles (<1 μm) and vapor phase species are transported by vapor phase and small particle diffusion. These particles are characteristically rich in flame-volatilized species that condense upon cooling in the bulk gas or in the gas boundary layer next to the tube. The diffusion mechanisms that are important with respect to the transport of vapor species and small particles include:

1. Fick diffusion - molecular level.
2. Brownian diffusion - particles suspended by a host liquid.
3. Eddy diffusion - turbulent systems.

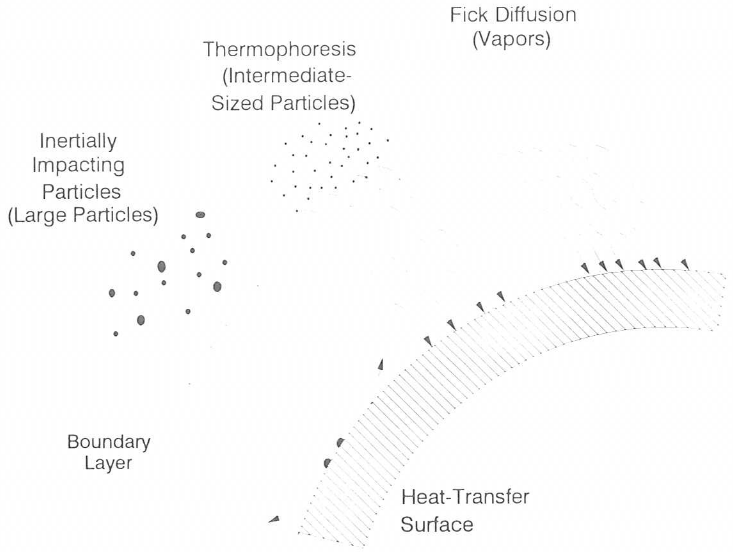


Fig. 4.8 Ash transport mechanisms to heat-transfer surfaces.

An additional transport mechanism which is important for the intermediate size range of particles is that of thermophoresis as illustrated in Fig. 4.8. Thermophoresis is a transport force that is produced as a result of a temperature gradient in the direction from hot to cold. This transport mechanism is important for particles < 10 μm. Electrophoresis is another transport mechanism that may be important with respect to the formation of deposits (ref. 6).

Larger particles, greater than 10 μm in diameter, may impact a heat transfer surface due to their inertia which prevents them from following the gas streamlines (e.g. around a tube). In other words, particles which inertially impact have sufficient inertial momentum to leave the gas streamlines and impact a surface. In contrast, the drag force on small particles is large enough to change the direction of the particles and keep them in the flow stream. The possibility of particle impaction on a surface depends upon the inertial momentum of the particle, the particle drag force, and the position of the particle in the flow stream. Gas velocity has a significant effect on the size of ash particles that will impact the surface. For example, in a gas turbine with a gas velocity on the order of 100 m/s, particles with diameters greater than 1 μm will impact. In typical utility boilers, the gas velocity is 10-25 m/s, and particles with diamters of 5-10 μm will impact.

The initial deposit layers formed when firing a coal that produces an abundance of intermediate and small sized particles is illustrated in Fig. 4.9. These coals characteristically contain low-levels of mineral grains and high levels of organically associated inorganic components. An initial white-colored layer consisting of particles less than 5 μm in diameter was formed on all sides of the tube. These particles were transported to the surface by mechanisms other than inertial impaction. The massive deposit on the upstream side of the tube is a result of particles greater than 5-10 μm transported to the surface by inertial impaction. As expected, inertial impaction accounts for the bulk of the deposit growth.

Figure 4.10 illustrates particle impaction efficiency (fraction of particles approaching the surface which impact) as a function of particle size for a heat-transfer turbe in cross flow (ref. 36). Note the significant effect of thermophoresis on the transport of intermediately sized particles and the dominance of inertial impaction for large particles.

4.4.2 Ash Particle Sticking and Adhesion

The factors that influence the adhesion of an ash deposit to a heat-transfer surface include:

1. Temperature of the steel surface.
2. Thermal compatibility between the deposited material and the heat transfer surface.

3. Chemical compatibility between the initiating particles and the heat transfer surface.
4. Surface tension of the initiating ash droplet.

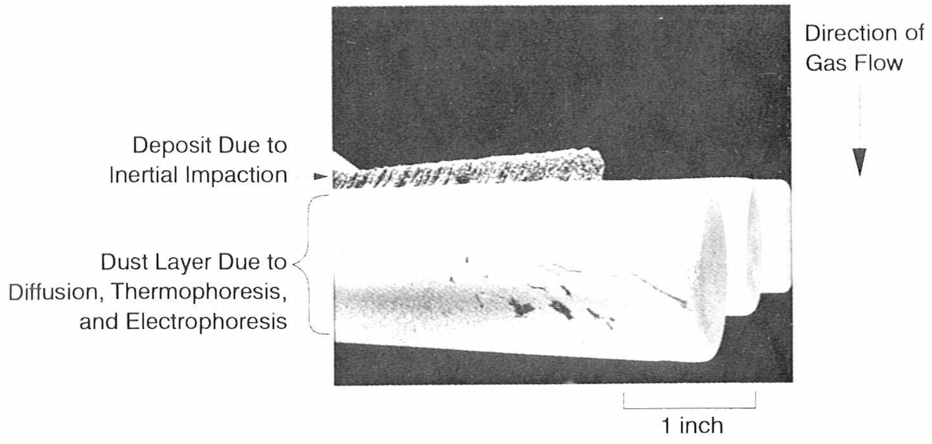


Fig. 4.9 Simulated heat-transfer surface from a 146,500-W (500,000 Btu/hr) pilot-scale combustor.

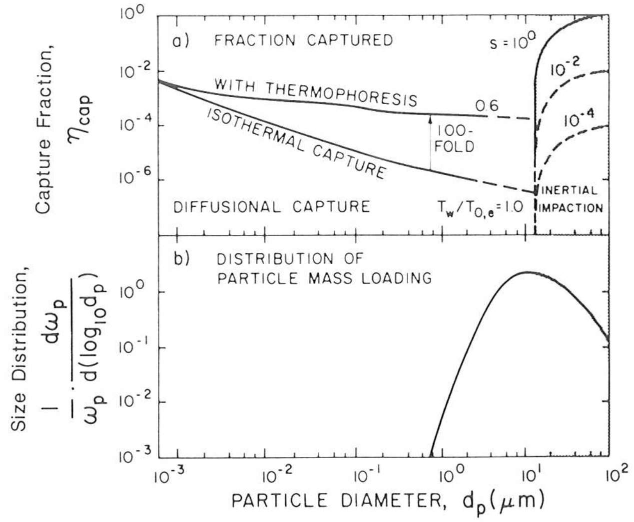


Fig. 4.10 Representative heat-exchanger tube fouling-rate conditions: (a) particle-size dependence of the capture fraction, η_{cap}, (b) size distribution of mainstream particle mass loading. Overall mass fouling rate will be proportional to the integral of the product of these two functions (ref. 36, published with permission).

In the high-temperature radiant section of a utility boiler, molten ash particles may impact on the waterwalls resulting in the formation of a deposit. The initiating layers next to the heat-transfer surfaces may contain condensed, flame-volatilized species, in the form of small particles, that are rich in alkali and alkaline earth sulfates. These particles are held in place by Van der Waals and electrostaic forces (ref. 6). Particles impacting this layer may incorporate some alkali and alkaline earth elements. The alkali and alkaline elements will cause the formation of lower melting point phases that can contribute to increased bonding to the surface.

The thermal and chemical compatibility between the steel surface and the deposit influences the deposit's ability to stick and remain during normal cycling of the utility boiler. If the thermal characteristics (*i.e.*, thermal expansion coefficients) of the heat-transfer surface and the depositing material are similar, the deposit will not shed easily when the unit is cycled. On the other hand, if the thermal expansion coefficients of the ash and the surface are different, the deposits will shed much more easily during cycling. The coefficients of thermal expansion of boiler steels, oxides, and silicates constituents are summarized in Table 4.6. The materials that have similar thermal expansion coefficients will likely form bonds that will not break during cycling the unit.

TABLE 4.6

Thermal Expansion Coefficients for Selected Materials (refs. 6, 29, 37)

Material	Linear Expansion Coefficient, 0-1000 C (in/in K x 10^6)	Material	Linear Expansion Coefficient, 0-1000 C (in/in K x 10^6)
Al_2O_3	8.8	Fireclay Refractory	5.5
MgO	13.5	K_2O-Fe_2O_3-SiO_2[b]	10.3
SiO_2		CaO-Al_2O_3-SiO_2[c]	4.5-8.3
Muilite	5.3	Na_2O-Fe_2O_3-SiO_2[d]	11.6-14.6
Spinel	7.6		
Soda-lime-glass	9.0	Fe-Oxides	8-10
Sodium Aluminosilicate glass[a]		Stainless Steel	16-18
$NaAlSi_2O_8$	7.0	Mild Steel	11-12
$NaAlSi_3O_8$	6.4		

[a] At temperature 2573 K. [b] K_2O = 16.67%, Fe_2O_3 = 16.67%, SiO_2 = 66.66% at room temp to 700 K.
[c] At 300-573 K expansion coefficient depends upon the composition.
[d] At 323-623 K expansion coefficient depends upon the composition.

Chemical bonding between the ash deposit and the steel surface provides for the formation of the strongest bonds. Good adherence is related to the level of metal oxide in the amorphous deposit material (glass). For example, the iron level in glass is a good indicator of the ability of the deposit to form a strong bond with a heat-transfer surface. Various indices have been developed that can predict the sticking propensity as described by Raask (ref. 6).

Detailed fundamental studies of factors that influence the sticking of coal ash slags to heat-transfer surfaces were conducted by Austin *et al.* (refs. 38-43). They developed a simplified apparatus to produce molten droplets of slag and allow them to fall and stick to a boiler steel coupon that was held at a controlled temperature. The information generated with this apparatus lead to an improved understanding of the factors that influence the sticking behavior of slag droplets on boiler steel surfaces. The factors include slag droplet composition, droplet temperature, nature of the steel surface, and steel temperature. The contact angle of the droplet was observed to decrease with increasing substrate or coupon temperature resulting in increased wetting of the surface. The strength of adhesion increased exponentially with substrate temperature. Mild steels exhibited an interaction of the glass or slag droplet with oxide layer on the steel, resulting in a strong bond. Ash droplet interaction with stainless steels exhibited poor wetting and low adhesion strengths up to 863 K. Limited chemical reaction occurred. Initial layers with high levels of Na_2SO_4 or NaCl decreased the sticking temperature. The adhesion force decreased as a result of decreasing substrate temperature and thermal cycling of the substrate temperature.

In further studies on the adhesion of ash particles to boiler steel substrates, a laminar flow furnace or drop-tube furnace system was constructed in order to simulate the ash-forming properties and residence times of full-scale combustors (ref. 7). In this laboratory apparatus a thin stream of coal is combusted in a tube heated to simulate the temperature history of a utility boiler. The resultant ash is accelerated through a constriction and impacted on a cooled boiler steel substrate. This system has been used to study deposit initiation (ref. 7, 8) as well as deposit growth and strength development (refs. 44, 45). For example, a recent study examined particles that form strong bonds with boiler surfaces (ref. 8). The strongly bonded particles were sheared from the substrate, and the adhesive strengths were measured. In addition, the particles were examined with a scanning electron microscope/microprobe in order to image and determine the chemical composition of the droplet. The particles that formed strong bonds included those rich in iron and silicon; iron and sulfur; iron, calcium and sulfur;

barium and sulfur; barium, strontium, and sulfur; and calcium and phosphorus. An example of particles that formed strong bonds with heat-transfer surfaces is illustrated in Fig. 4.11.

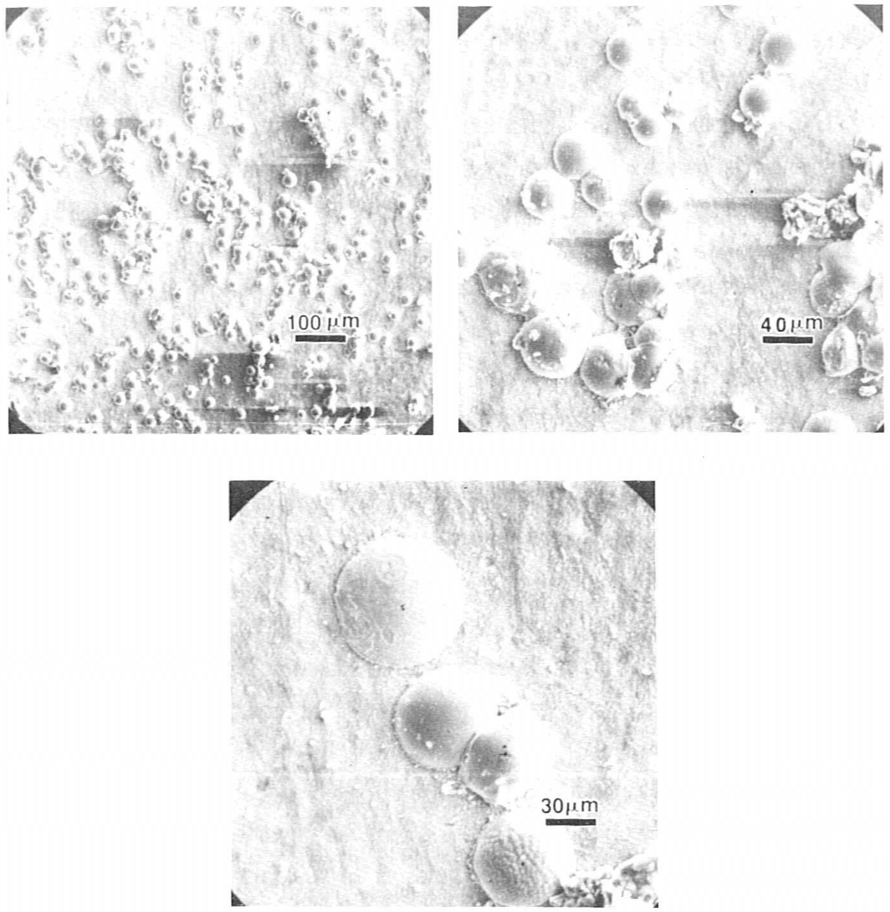


Fig. 4.11 San Miguel Texas lignite ash particles sticking to oxidized boiler steel substrates held at 773 K (ref. 43).

4.5 DEPOSIT CHARACTERISTICS AND GROWTH

4.5.1 Deposition Phenomena in Utility Boilers

The characteristics of a deposit depend upon the chemical and physical characteristics of the intermediate ash species, geometry of the system (gas flow patterns), gas temperature, gas composition, and gas velocity. Figure 4.12 illustrates ash

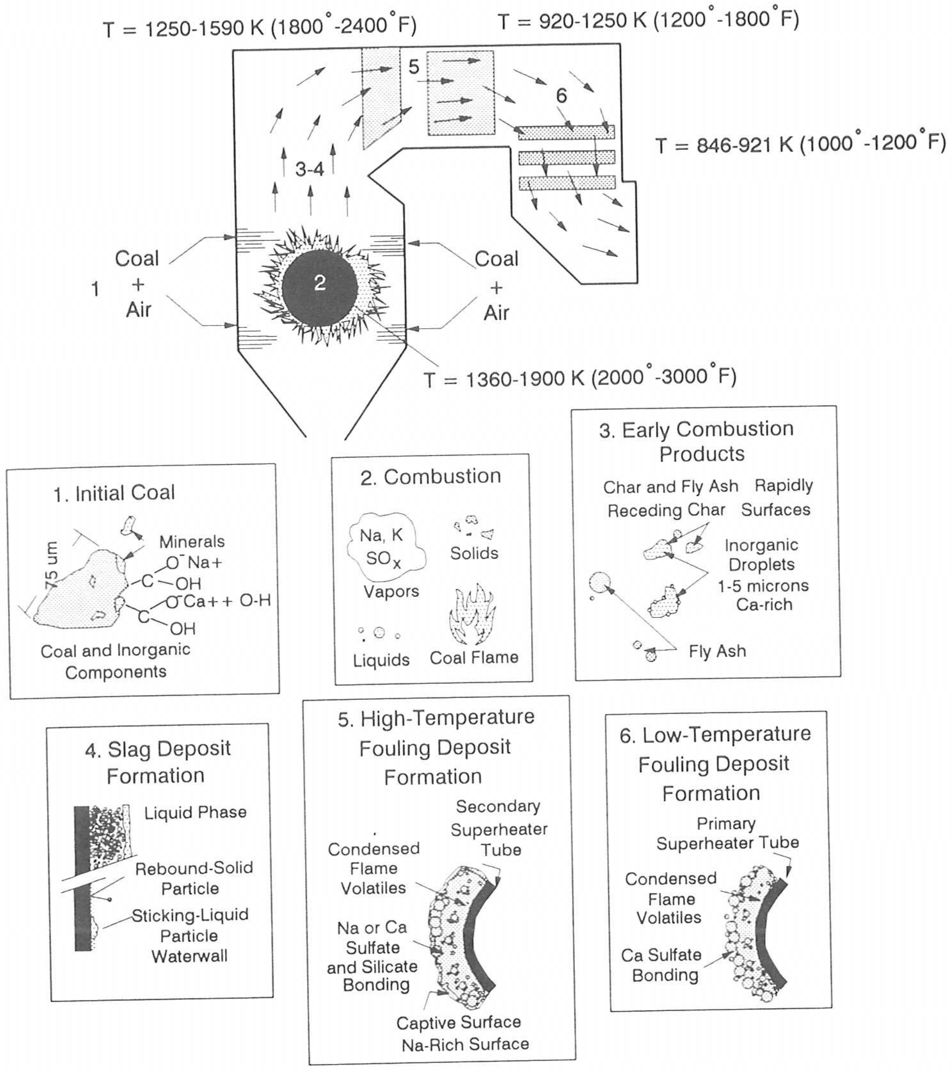


Fig. 4.12 Ash deposition phenomena in utility boilers.

deposition phenomena in utility boilers. Deposits that form in the radiant section are called slag deposits. Deposits that form in the convective pass on steam tubes are called fouling deposits. Slag deposits are exposed to radiation from the flame, and are usually associated with a high level of liquid phase components. Silicate liquid phases are typically the most prevalent, although the deposit may also contain moderate to high levels of reduced iron phases. Initial layers of slag deposits may consist of very fine particulate which can be highly reflective. Fouling deposits form in the convective passes of utility boilers and, in most cases, do not contain the high levels of liquid phases that are usually associated with slagging type deposits. Rather, fouling deposits contain low levels of liquid phases (e.g. a combination of silicates and sulfates) that bind the particles together. The formation of these deposits on heat-transfer surfaces can significantly reduce heat transfer. The heat transfer through a deposit is related to the temperature, thermal history, and physical and chemical properties of the deposited material. Properties which have a significant effect on heat transfer include the thermal conductivity, emissivity, and absorptivity.

4.5.2 Slagging Deposits

The factors that contribute to the formation of slag deposits include (1) gas flow patterns resulting in impacting and sticking particles, (2) low-excess air conditions causing localized reducing conditions which increase the quantity of low melting point phases, (3) the formation of a molten captive deposit surface that becomes an efficient collector of impacting particles, and (4) an increase in gas temperature caused by less efficient heat transfer. Hatt *et al.* (ref. 46) have classified slag deposits from utility boilers into four principal types which include (1) metallic slags that have a metallic luster and are usually associated with the combustion of pyrite-rich coals (reducing conditions cause the separation of the metallic portion from the other slag components), (2) amorphous, glassy slag that is relatively homogeneous with a high degree of assimilated ash particles, (3) vesicular slags that consist of amorphous slags that contain trapped bubbles and have a sponge-like appearance, and (4) sintered slag deposits that are only partially fused. The principal impact of these deposits is to reduce heat transfer by changing both the radiative properties (emissivity) and thermal resistance (thermal conductivity) of the heat transfer surface. The physical state of the deposit has a significant effect on the heat-transfer properties. For example, a molten deposit will have higher emissivity than a sintered deposit.

The primary particle bonding or sintering mechanisms are dominated by silicate liquid phases. In addition, in high-pyrite coals, iron-rich silicates, FeO, and FeS can play a role in deposit initiation and growth. The initial layers of slag deposits are usually rich in small, lightly sintered particles along with larger particles that have impacted the surface and stuck. In some cases, heat transfer can be significantly reduced by the formation of a highly reflective ash layer in the radiant section. This reflective ash layer is a result of the transport of small particles to the heat-transfer surface and is a characteristic of coals that produce an abundance of small particles. These initial layers are composed of simple oxides, such as CaO, MgO, FeO, Fe_2O_3, and Fe_3O_4, and complex glassy silicate phases that are stable in the radiant section of the boiler.

The distribution of phases that cause ash deposition are best illustrated by the examination of deposits collected from a utility boiler. Samples were collected from a utility boiler at locations illustrated in Fig. 4.13 while the unit was off-line. The temperatures are noted at the locations where samples were obtained when the unit was operated at 460 MW (ref. 47). The unit was cycled to lower load conditions so the temperatures illustrated were the highest gas temperatures experienced by the deposits.

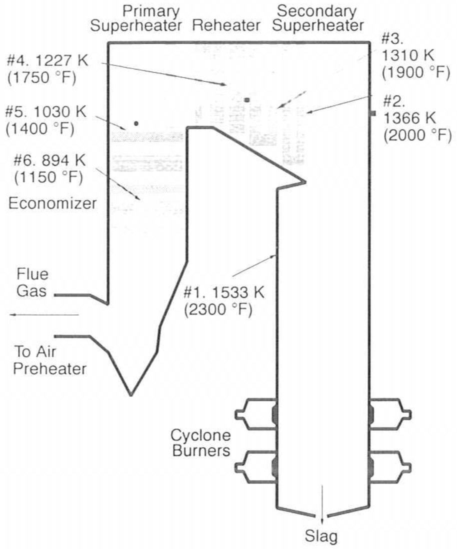


Fig. 4.13 Location of samples collected while unit was off-line. The temperatures are the maximum temperatures to which the deposits were subjected.

The coal fired when these deposits were formed was a subbituminous coal from Wyoming. The bulk chemistry of the deposit was determined and plotted as a function of the maximum temperature as shown in Figs. 4.14 and 4.15. The figures show several trends between the composition of the deposit and the temperature of the surrounding gas. The most dramatic trend is the abrupt change in the concentration of sulfur between Samples 2 and 3 (Fig. 4.14). The change indicates that above about 1400 K sulfur is not thermodynamically stable in the condensed form and cannot participate in the formation of the deposits above 1400 K. The dominant phases in the radiant section of the boiler were the silicates. The sulfur-bearing phases are not a significant factor in slagging problems.

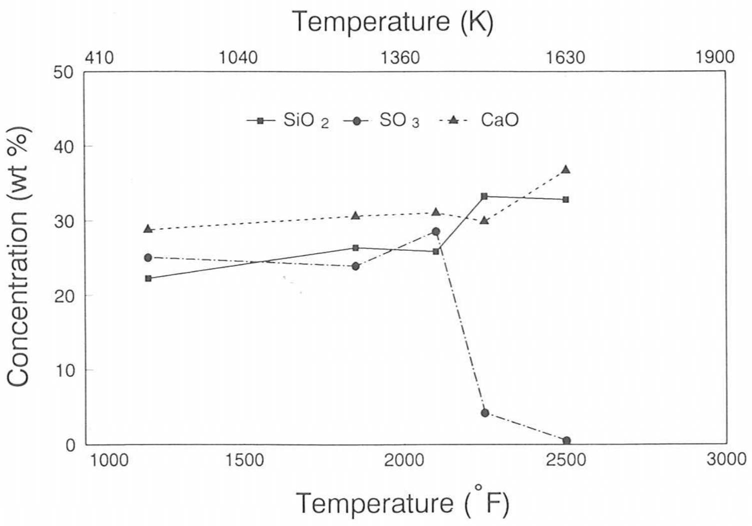


Fig. 4.14 SiO_2, CaO, and SO_3 concentrations in the ash samples versus temperature for off-line samples. SiO_2 and CaO values are presented in an SO_3-free basis.

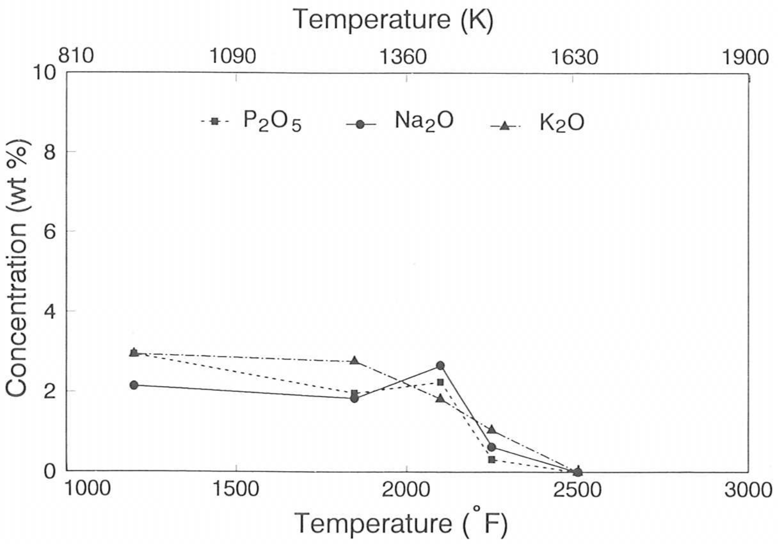
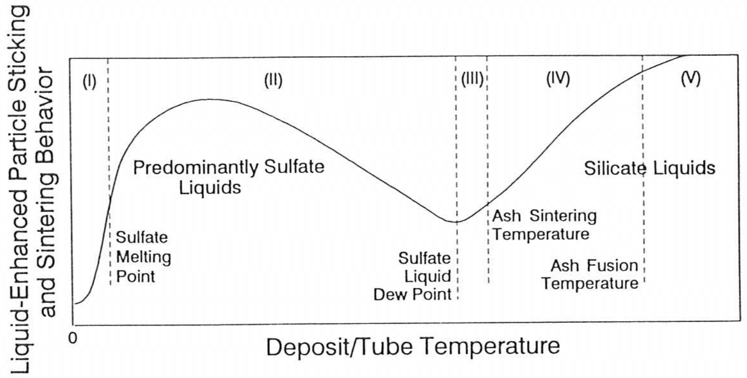


Fig. 4.15 The concentrations of P_2O_5, Na_2O, and K_2O versus temperature for samples collected off-line, SO_3 free.

4.5.3 Fouling Deposits

Fouling problems in utility boilers have been classified into two principal types: high temperature fouling and low temperature fouling (ref. 47). This distinction is needed since the bonding mechanism of the deposits differ. Figure 4.16 illustrates the type of liquid components present as a function of temperature (ref. 48). At lower temperatures, sulfates dominate, while at higher temperatures, silicates are more prone to produce liquids. In high-temperature fouling, the bonding of particles is due to silicate liquid phases and in low-temperature fouling, the bonding is a result of the formation of sulfates. Condensed sulfur species, principally in the form of $CaSO_4$, are stable and form the matrix or bonding material in the low-temperature deposits.



Deposition Regimes:
(I) Dry-Sticking Regime: (No Glue)
(II) Vapor or Thermophoretically Deposited Liquid Glue
(III) Glue Produced by Heterogeneous Chemical Reactions at Vapor/Ash Interface
(IV) Ash Particle Softening on Impact
(V) Wet Limit (Sticking Coefficient Nearly Unity)

Fig. 4.16 Distribution of liquid phases as a function of deposit temperature (ref 48).

(i) *High-Temperature Fouling*. High-temperature fouling occurs in regions of the utility boiler where temperatures exceed the stability of the sulfate-bearing phases. In combustors burning coals that contain high levels of alkali and alkaline earth elements, high-temperature fouling can be a significant problem. In most cases, the innermost layers consist primarily of small particles, rich in flame-volatilized species such as sodium and sulfur, which are transported to the surface by vapor phase diffusion and thermophoresis as shown in Fig. 4.17. Larger particles also impact the surface. The initial deposit layers may provide a sticky surface for trapping inertially impacting particles which are not sticky. In addition, the initial layers may provide fluxing materials that will

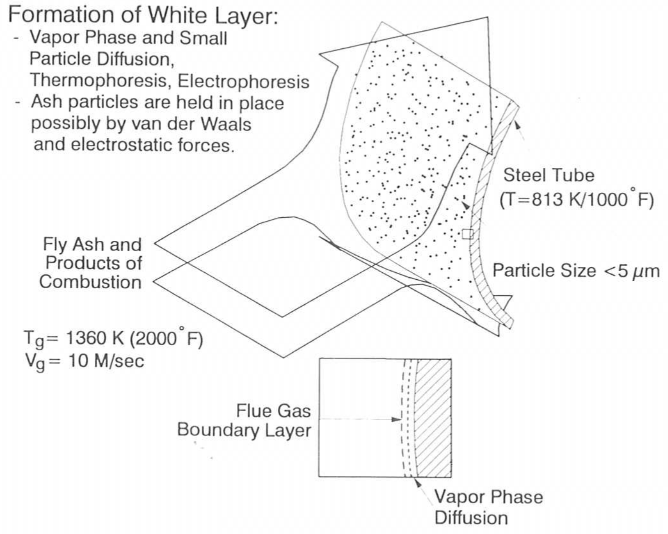


Fig. 4.17 Formation of initial deposit in fouling deposits.

cause larger particles to melt. Figure 4.18 illustrates particles that have bonded to the heat-transfer surface. These particles provide sites for continued deposition to form islands of particles. These initial islands are the precursors of the more massive upstream deposits that form in the secondary superheater and reheater sections of a utility boiler. Coatings also form on the surfaces of entrained ash particles as a result of the condensation and reaction of flame-volatilized species to form a molten or plastic surface. Condensation on surfaces of deposited ash particles can also occur. Figure 4.19 shows particles on the inner layers of ash deposits that have coatings of calcium and sodium sulfate rich material. These "puddles" of liquid phase material contribute to the thickening of bonds between particles. As a result of the insulating effect of the deposit layer on the tube, the outer layers of the deposit are formed at higher temperatures (Fig. 4.20). The higher temperature causes melting and interaction of the particles to from a liquid phase as shown in Fig. 4.21. Once a liquid phase has formed on the outside of the deposit, it becomes an efficient collector of ash particles, regardless of the individual melting characteristics of the particles.

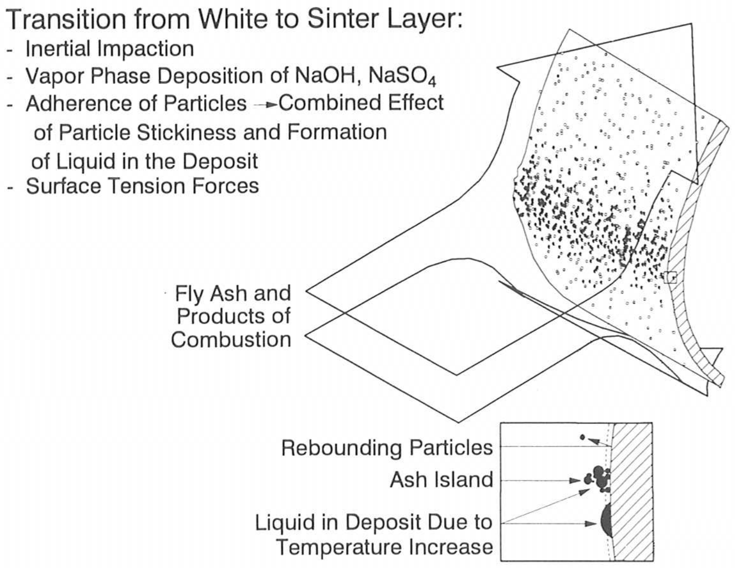


Fig. 4.18 Formation of transitional deposit layers in fouling deposits.

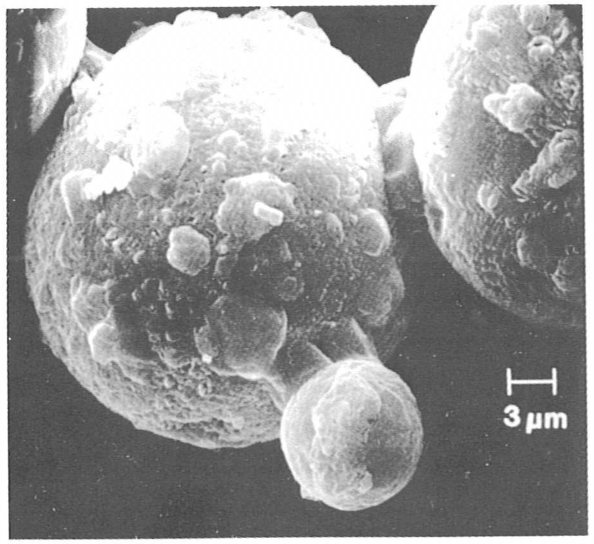


Fig. 4.19 Particles on the inner layers of ash deposits that have coatings of calcium and sodium sulfate-rich material.

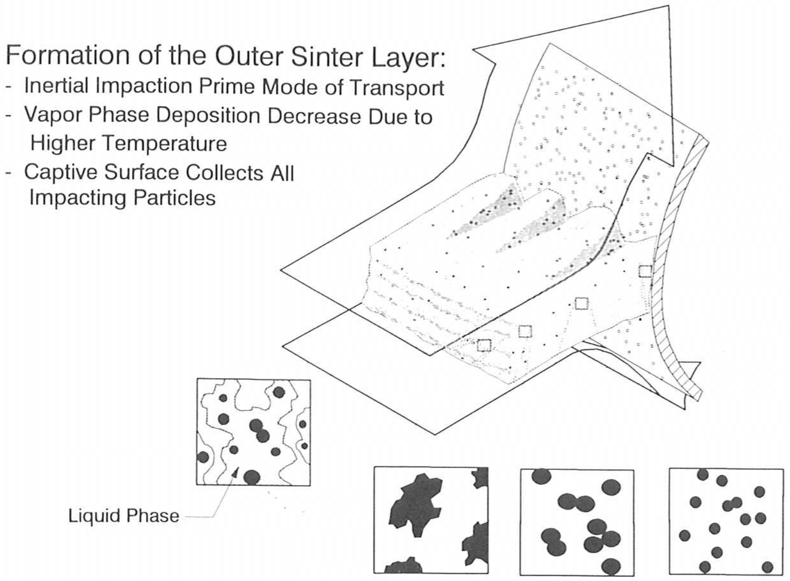


Fig. 4.20 Formation of outer layers in a fouling deposit.

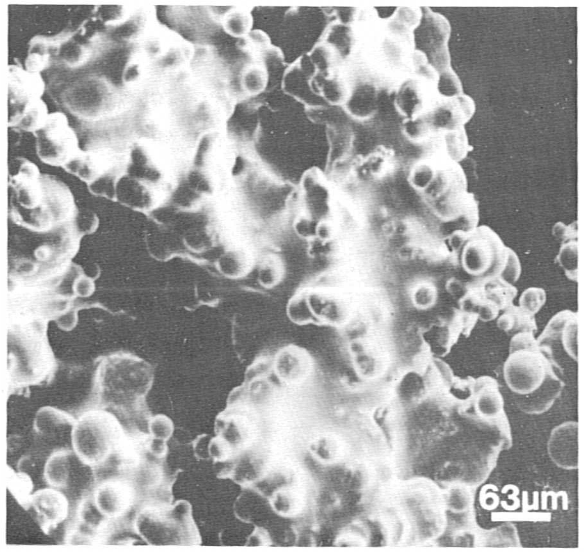


Fig. 4.21 Captive liquid surface in a high-temperature fouling deposit.

(ii) *Low-Temperature Fouling*. Low-temperature ash deposition occurs at temperatures in the range of 920-1250 K as shown in Fig. 4.22 (ref. 47). In systems

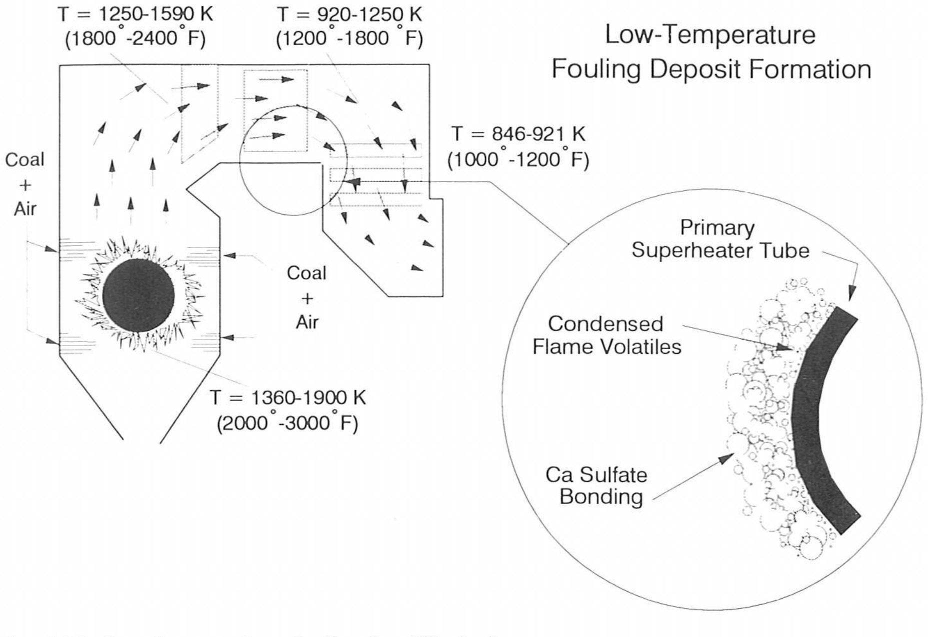


Fig. 4.22 Low-temperature fouling in utility boilers.

which exhibit low temperature fouling, the sulfate phases dominate the matrix or bonding mechanism between particles. Detailed examination of deposits (ref. 49) showed high levels of calcium in the deposits. Formation is dependent upon the availability of small calcium oxide particles and the process of sulfation. Figure 4.23 illustrates the morphology of deposits that form in the reheater and primary superheater regions of a utility boiler owing to the prevailing gas flow patterns. Based on detailed field testing to determine the mechanism by which low-temperature deposits form, Hurley *et al.* (ref. 47) identified that the deposit characteristics are related to the size and composition of the entrained ash. Samples were collected that represent the upstream (windward) and downstream (backside of the tube) deposits. In all cases, the sulfation process occurred after the particles were deposited; very little sulfation took place while the particles were entrained in the gas stream.

The initial layer of upstream deposits, called upstream enamel, formed on the surface of sacrificial probes in a temperature range between 1060-1370 K. Microscopic examination of this enamel layer indicated that it consisted mainly of particles with aerodynamic diameter $< 3\ \mu m$ that were highly sulfated. This layer results from thermophoresis/electrophoresis or simple diffusion of small particles. The upstream reheater deposits formed in the temperature range between 1170 and 1370 K as a result of inertial impaction of particles >10 μm. Once the particles were deposited, sulfation of those particles occurred resulting in the development of deposit strength. The upstream deposits were massive and began as islands that continued to enlarge. This result is based on work conducted using probes that could be cross-sectioned in order to determine how the initial layer was formed.

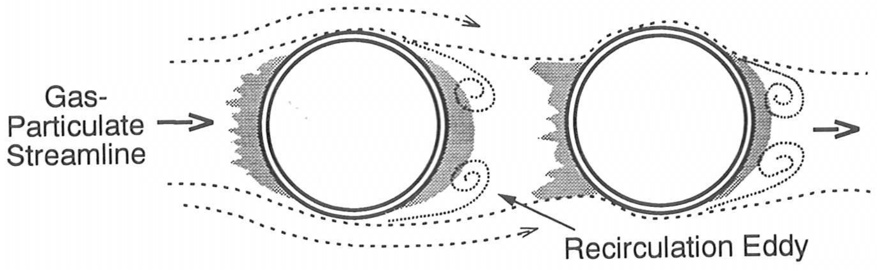


Fig. 4.23 Low-temperature fouling deposits.

Downstream deposits may form on all banks of tubes in the convective pass. Detailed examination of these deposits indicates that the particle sizes that contribute to their formation have aerodynamic diameters < 10 μm. The mechanism important for those particles is believed to be eddy impaction. Drag forces on particles < 10 μm in aerodynamic diameter should be sufficient to cause them to follow the eddies, resulting in impaction on the backside of the tube.

The particle-size composition distribution of the entrained ash was compared with the particle sizes of the ash in fouling deposits. The results showed that the compositions of the > 10 μm sized particles are similar to the compositions of the inertially impacted ash particles on the upstream side of the tube. Similar agreement in composition was found between particles < 3 μm and the enamel layer, and between particles < 10 μm and the downstream (backside) deposits. Table 4.7 summarizes the mechanism of transport and temperature ranges that lead to low-temperature deposit formation.

TABLE 4.7

Summary of Convective Pass Deposits

Type	Temp., K	Mechanism	Aerodynamic Diameter
Conventional	above 1280	Inertial Impaction	>10 μm
Upstream Reheater	1170-1370	Inertial Impaction	>10 μm
Upstream Enamel	1060-1370	Small Particle Diffusion/ Thermophoresis	<3 μm
Downstream	All banks	Eddy Impaction	<10 μm

4.6 PROPERTIES OF DEPOSITS

4.6.1 Deposit Strength Development

The development of deposit strength is due primarily to sintering or densification of the deposit. Sintering may occur by several mechanisms as discussed in Kingery *et al.* (ref. 29). Liquid phase or viscous flow sintering appears to be the dominant sintering mechanism for ash deposits and will be the principal focus of this section. Other mechanisms such as solid state sintering may also be involved, but to a lesser extent.

Viscous flow is illustrated in Fig. 4.24, where two particles are beginning to sinter. The sintering potential depends on both the amount and the physical properties (e.g. viscosity) of the liquid phase. In addition, the liquid phase can be either reactive or nonreactive with respect to solid components in the melt. Viscous flow sintering with a reactive liquid phase results in the formation of large amounts of liquid. There is an appreciable solubility of the solid phases in the liquid and good wetting of the solid by the liquid. Slagging deposits often sinter by viscous flow with a reactive liquid phase. Sintering times are usually on the order of 2-3 hours. On the other hand, viscous flow sintering with a nonreactive liquid phase does not lead to dissolution of the solid components. This type of sintering may play a role in the strengthening of low-temperature fouling deposits where sulfates bond silicate particles together with little or no reaction between the silicate and the sulfate phases. Sintering of these deposits by viscous flow of a nonreactive liquid is expected to take significantly longer than the time required for the sintering of slagging deposits since the liquid must first accumulate as a result of sulfation reactions and/or condensation. Solid state sintering may also play a role in the densification of low-temperature fouling deposits.

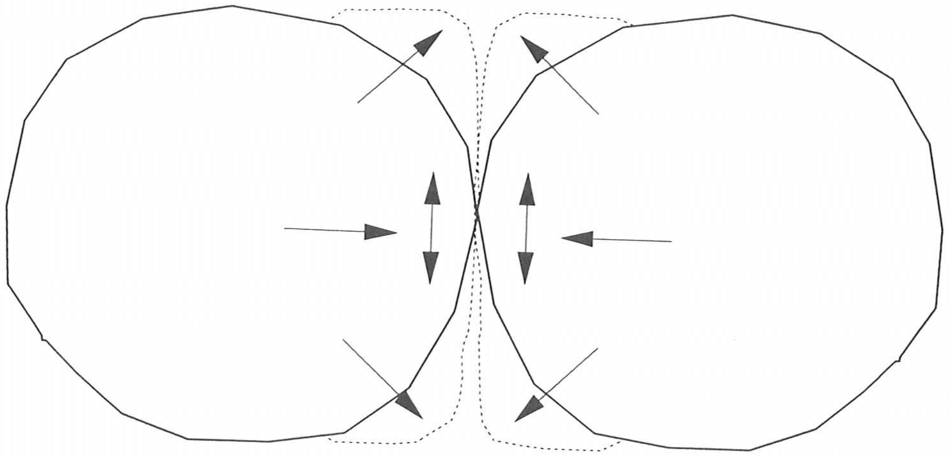


Fig. 4.24 Viscous flow sintering of two particles (direction of arrow indicate the flow of mass).

The driving force for densification is derived from the capillary pressure of the liquid phase between particles. When two particles that are coated with a liquid phase are in contact with each other, the interparticle space becomes a capillary in which substantial capillary pressure can develop. For example, in silicate systems containing capillary diameters between 0.1 and 1 μm, the pressure can range from 1.2-12.1 MPa (ref. 29). The capillary pressure increases densification by:

1. Rearranging the particles to increase packing effectiveness,
2. Increasing the number of contact points between particles,
3. Promoting the dissolution of smaller particles to produce larger particles (Ostwald ripening),
4. Transferring material away from particle contact points to bring particle centers closer together.

The reactivity and liquid forming propensity of the deposited ash particles can be approximated from the base-to-acid ratio distribution of the particles. Basic components include network modifiers such as calcium or sodium. Acidic components include species such as silica which are network formers. A mixture of acidic and basic components tends to react to form low melting point species. Therefore, a deposit which contains both acidic and basic particles has a high potential for liquid phase formation. In contrast, a deposit consisting of particles which are either all basic or all acidic has less potential

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for liquid phase formation. Particles which contain both acidic and basic components may also melt at low temperatures and contribute to liquid phase sintering.

Crystallization is another factor which may affect the densification process. The formation of crystals from a liquid phase reduces the amount of liquid. The composition of the residual liquid, and hence its physical properties, may also change as components are selectively removed by crystallization. The formation of the crystals or solid grains themselves may also affect the local density and strength of the deposit. In general, crystallization tends to slow the densification process and weaken the deposit.

Relationships are currently being developed between the chemical composition and physical properties of coal ash slags. Two key physical properties for viscous flow sintering are the viscosity (η) and the surface tension (γ). Nowak and Benson (ref. 50) performed experiments with homogeneous slags in order to relate the base-to-acid ratio (chemical composition) to the surface tension-to-viscosity ratio (γ/η). Figure 4.25 is a plot of the measured γ/η as a function the base-to-acid ratio which indicates that γ/η is clearly dependent on the chemistry of the system. A linear relationship was obtained from experiments performed in air, while an exponential increase was observed for experiments performed in a CO/CO_2 environment. The rapid change for the CO/CO_2 experiments

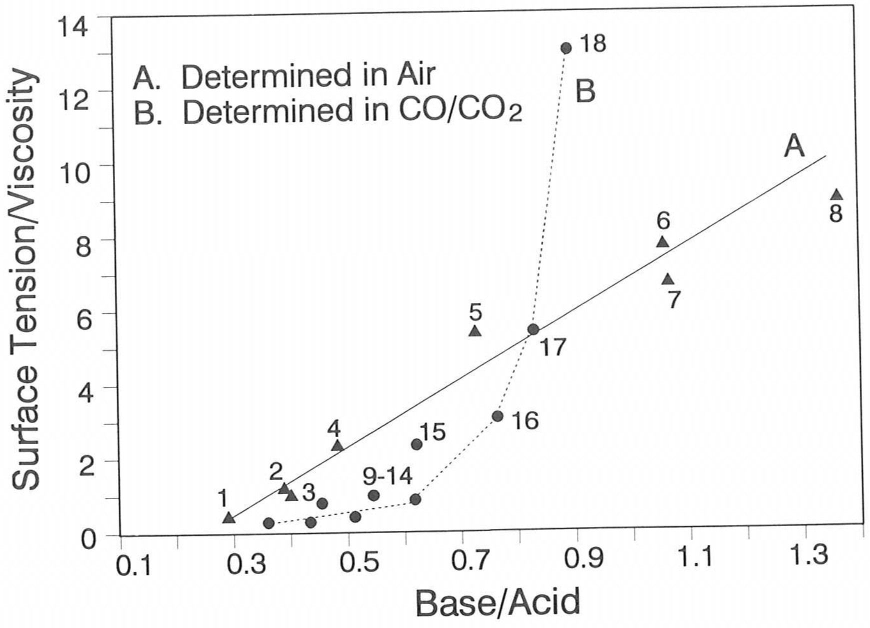

Fig. 4.25 Measured surface tension/viscosity ratio versus base-to-acid ratio for homogeneous slags determined in air and a CO/CO_2 atmosphere above the temperature of activated viscosity (ref. 50).

was due to a change in the oxidation state of the iron which decreased the viscosity of the liquid. Compressive strengths were also determined for selected homogeneous slag pellets that were sintered in air at 1370 K as shown in Fig. 4.26. The pellet strength increased with increasing γ/η, as expected for viscous flow sintering.

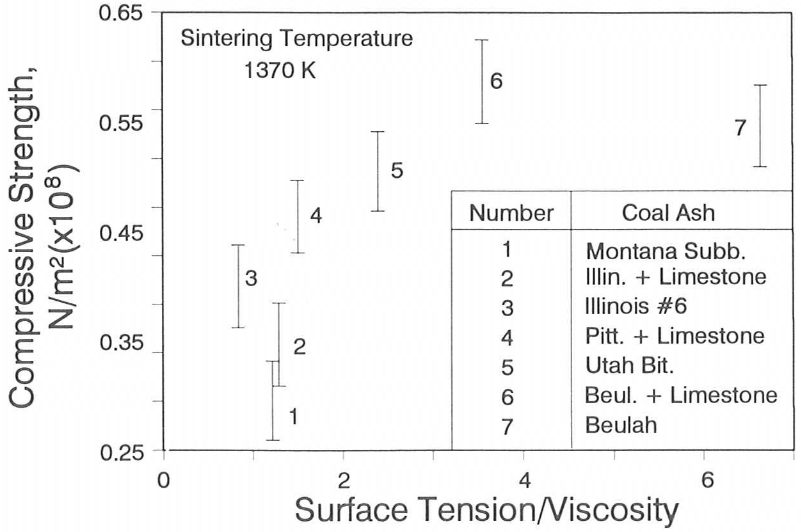

Fig. 4.26 Compressive strength of pellets sintered at 1370 K in air versus the surface tension/viscosity ratio for selected homogeneous coal ashes (ref. 50).

4.6.2 Deposit Thermal Properties

The heat-transfer in a utility boiler involves radiation, convection, and conduction as illustrated in Fig. 4.27. Heat is transferred to the deposit (or tube) surface by both radiation and convection. The heat is then conducted through the deposit and tube wall and transferred to the cooling fluid inside the tube. The properties of the deposit that influence the heat transfer are the emissivity and the thermal conductivity.

Wall *et al.* (ref. 51) reviewed the effect of deposit properties on the emissivity and the thermal conductivity of the deposit. The emissivity was affected by the physical structure, shape, and chemical composition (color) of the deposit. Emissivity of coal ashes decreased with temperature at lower temperatures, and then increased sharply at higher temperatures as sintering and fusion occurred. Particle size was the most dominant variable which affected the emissivity of unsintered samples.

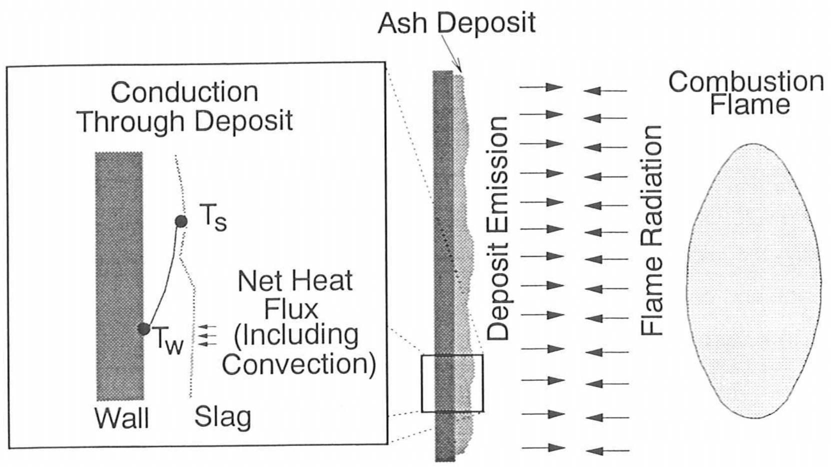

Fig. 4.27 Heat transfer through a deposit in a utility boiler.

The thermal conductivity of the deposit is also related to the physical structure and chemical composition of the deposit. A deposit that is highly porous and composed of insulating materials will have a low thermal conductivity, while low porosity materials containing iron will have higher thermal conductivities. Figure 4.28 shows thermal conductivities for deposits as measured by Wall *et al.* (ref. 51) and Benson *et al.* (ref. 52).

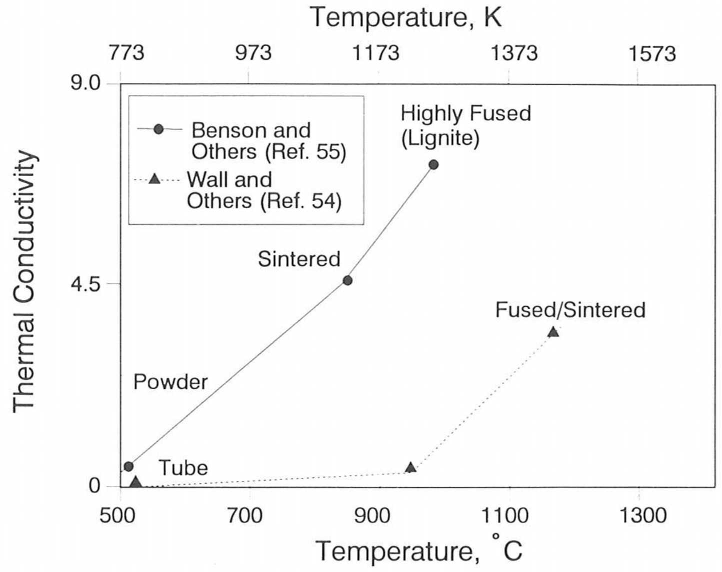

Fig. 4.28 Thermal conductivity of deposits having different characteristics.