

## DEPOSIT CONSTITUENT PHASE SEPARATION AND ADHESION

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The initial deposit material on coal fired boiler tubes consist largely of silicate, sulphate and iron oxide particles. The fused silicates and molten sulphates form immiscible phases at high temperatures first on the micro-scale in individual particles and subsequently as separate layers in the deposit. The adhesion of ash deposit constituents to boiler tubes starts with the small particle retention as a result of the van der Waals, electrostatic and liquid film surface tension forces. Subsequently a strong bond will develop between the oxidized metal surface and iron saturated layer of ash deposit.

The pulverized coal fired boilers at electricity utility power stations are designed for "dry" ash operation where the bulk of mineral matter residue is removed in the electrical precipitators in the form of particulate ash. However, it is inevitable that some deposits of sintered ash and semi-fused slag form on the heat exchange tubes and between 20 and 30 per cent of coal ash is discharged from the combustion chamber as clinker. The high temperature cyclone fired boilers are designed for "wet" ash operation and up to 80 per cent of coal ash is discharged from the furnace as molten slag.

The build-up of sintered ash and fused slag deposits depends chiefly on the rate of ash particle impaction and the adhesive characteristics of the collecting surface. The initial deposit on the heat exchange tubes in pulverized coal fired boilers consists of ash particles of diameter ranging from less than 0.1  $\mu\text{m}$  to 100  $\mu\text{m}$ . Subsequently the deposited ash may be re-entrained in the flue gas or it may form first a sintered matrix and later a fused slag deposit chiefly by viscous flow. For the deposit formation the ash particles must be first held at the collecting surface and subsequently the deposit matrix bonded to the boiler tubes by adhesive forces sufficiently strong to overcome the gravitational pull, boiler vibration and eventually the sootblower jet impaction. This work sets out to examine the adhesive characteristics of different constituents of the flame heated ash and the formation of sintered deposits and slag bonded to the heat exchange tubes.

### INITIAL DEPOSIT CONSTITUENTS

The mineral matter in coal consists chiefly of silicate, sulphide, carbonate species, and chlorides and organo-metal compounds associated with the fuel substance (1,2). The silicate mineral particles vitrify partially or completely, in the pulverized coal flame (3), and thus the silicate ash fraction of the initial deposit consists of particles of variable amounts of a glassy phase and crystalline species (4).

The sulphide, carbonate, chloride and organo-metal species dissociate and oxidize in the flame. The oxides may remain as discrete particles, chiefly iron oxide (magnetite), can dissolve in the glassy phase of silicates, and a fraction of calcium and sodium oxides are sulphated (5). Thus the initial deposit material will contain some calcium, sodium and potassium sulphate. The latter originates from the release of potassium in the flame heated aluminosilicate particles (6).

The relative concentrations of flame heated ash constituents, namely silicates, iron oxide and sulphate can be estimated from the ash analysis. However, the composition of the initial deposit material can be markedly different as a result of selective deposition. In particular, the deposit material can be enriched in sulphate as shown in Fig. 1. The relative concentrations of different deposit constituents were obtained by analysing the material on a cooled metal tube probe inserted in boiler flue gas for short, 2 to 15 minute duration (7). The sulphate content of the flue gas borne ash and probe deposits in a cyclone fired boiler was higher than that in the pulverized coal fired boiler ash and deposits. This was because in cyclone boilers the bulk of silicate ash is discharged as molten slag but the residual ash is relatively rich in sulphate.

The rate of alkali-metal sulphate deposition will decrease when the temperature of collecting target surface exceeds 1075 K as shown in Fig. 2. The decrease in the deposition of alkali-metal sulphates is related to the concentration of the volatile alkali-metals in the flue gas and the saturation vapour pressure of sodium and potassium sulphates (8). The initial deposit on cooled surfaces contains a small amount of chloride as shown in Fig. 2.

In a reducing atmosphere the deposit material may contain iron sulphide (FeS) formed on dissociation of coal pyrite mineral. This is likely to occur on the combustion chamber wall tubes near the burners where the reaction time is short, below one second, for oxidation of FeS residue to the oxide. It has been suggested that calcium sulphide (CaS) may also be present in the ash material deposited from a reducing atmosphere gas stream as a result of sulphidation of calcium oxide (9).

#### THERMAL STABILITY OF SULPHATES AND IMMISCIBILITY WITH SILICATES

Bituminous coals usually leave a highly silicious ash on combustion. That is, fused aluminosilicates constitute an acidic media at high temperatures that is capable of absorbing large quantities of basic metals in the form of oxides, chiefly those of sodium, calcium and magnesium. At lower temperatures the corresponding sulphates are thermodynamically more stable in the presence of sulphur gases. The equilibrium distribution of alkaline oxides between molten sulphates and fused silicates at different temperatures can be calculated from the appropriate thermodynamic data. However, the residence time of the flame borne mineral species before deposition is short and the alkali-metal distribution does not reach the equilibrium state.

The fused silicate particles will absorb the flame volatilized sodium to the depth of about 0.05  $\mu\text{m}$  (10), and the remainder is converted to sulphate partly in the flue gas and partly at the surface of ash particles. The distribution of sodium in the silicate and sulphate phases can be expressed in a form:

$$m_{\text{sul}} = m_o - kw^{2/3} \quad \dots 1)$$

$$\text{where } m_{\text{sil}} + m_{\text{sul}} = m_o \quad \dots 2)$$

$m_{\text{sil}}$ ,  $m_{\text{sul}}$  and  $m_o$  denote the amount of sodium in silicate and sulphate fractions, and the total sodium in ash respectively;  $k$  is a constant and  $w$  is the ash content of coal. When the sodium to ash ratio is below 1 to 100 the bulk of sodium is captured by the silicate particles and equation 2 reduces to:

$$m_{sil} \approx m_o$$

... 3)

and consequently the amount of sodium available for the formation of sulphate is small.

The molten sodium sulphate/sodium silicate system of composition  $Na_2SO_4/Na_2O-SiO_2$  has one liquid phase at 1475 K, but as the proportion of silica increases, the melt separates into two layers (11,12). The change from the miscible to immiscible phase of the system has been explained by alterations in the silicate structure as the ratio of  $Na_2O$  to  $SiO_2$  decreases. In more basic, less viscous melts, the silicate ions exist in the form of  $SiO_4^{4-}$  tetrahedrons which have the same mobility as sulphate ions, and thus homogeneity of the system is to be expected. As the silica content is increased the complexity of the silicate structure reaches a point where the silica anions become relatively immobile for a separation of sulphate from silica to take place.

The miscibility of the corresponding potassium sulphate-silicate system has been studied by the usual crucible method as well as by a technique of a hanging droplet (13). The droplets of potassium sulphate/silicate mixtures, 3 mm in diameter, were suspended from 0.5 mm platinum wire which had a semi-spherical head 1.5 mm in diameter. Separation of the silicate (internal) and sulphate phases in the droplets can be observed directly in the Leitz heating microscope which is used, in its conventional mode of operation, to assess the fusion characteristics of coal ashes (14). Fig. 3 shows the two phase separation of  $2K_2SO_4-K_2O-2SiO_2$  system at 1575 K where the outside envelope is the transparent sulphate phase through which the platinum wire heats (top) and a globule of molten silicate (bottom) can be seen. As the temperature was increased to 1725 K the two phases became miscible because of the increased solubility of sulphate in the silicate melt at the higher temperature.

The  $K_2SO_4-K_2O-SiO_2$  phase diagram is depicted in Fig. 4 which shows that the system is miscible at 1575 K when the molar ratio of  $K_2O$  to  $SiO_2$  is above 0.5. As in the corresponding sodium sulphate/sodium silicate system, less basic melts separate into two immiscible liquids. This is the case with most coal ash slags where the molar ratio of basic oxides (sum of  $Na_2O$ ,  $K_2O$ ,  $CaO$  and  $MgO$ ) to  $SiO_2$  is well below 0.5. Exceptions to this are the sodium and calcium rich ashes of some lignite and non-bituminous coals, which can have sufficient amounts of alkalis to form a single phase melt of miscible sulphates and silicates at high temperatures.

#### ADHESION BY VAN DER WAALS AND ELECTROSTATIC FORCES

The ash particles deposited on boiler tubes are initially held in place by surface forces, i.e. van der Waals and electrostatic attraction forces. Van der Waals forces become important when molecules or solid surfaces are brought close together without a chemical interaction taking place. For a hemispherical particle of radius ( $r$ ) held at a distance of nearest approach ( $h$ ) from a plane, the resultant forces ( $F$ ) is given by:

$$F = \frac{Ar}{6h^2} \quad \dots 4)$$

where  $A$  is the Hamaker constant (15).

Equation 4 applies over short distances, up to 150 Å ( $1.5 \times 10^{-8}$  m) and for longer distances the "retarded" van der Waals forces decay rapidly (16). An equation based on the dielectric properties of solids for the retarded

van der Waals forces ( $F'$ ) between a sphere of radius ( $r$ ) at the distance ( $h$ ) from a flat surface is (17):

$$F' = \frac{2B\pi r}{3h^3} \quad \dots 5)$$

where  $B$  is the appropriate constant for the given material.

The changeover from the unretarded to retarded van der Waals forces occurs at a distance of about  $150 \text{ \AA}$  ( $1.5 \times 10^{-8} \text{ m}$ ), and the corresponding value of the Hamaker constant ( $A$ ) in equation 4 was found to be  $10^{-19} \text{ N}$  (Newton), and that of the Lifshitz constant ( $B$ ) in equation 5 was  $8.9 \times 10^{-29} \text{ N m}$  (16,18). These values have been used to compute the ratio of van der Waals forces to the gravitational force on small ash particles approaching a flat surface.

The gravitational force ( $F_g$ ) on an ash particle of radius ( $r$ ) and the density ( $D$ ) is given by:

$$F_g = \frac{4\pi r^3 Dg}{3} \quad \dots 6)$$

where  $g$  is the gravity acceleration constant ( $9.81 \text{ m s}^{-2}$ ). Thus, the ratio ( $F_r$ ) of the short distance van der Waals forces ( $F$ ) to the gravitational force ( $F_g$ ) on a particle is:

$$\frac{F}{F_g} = F_r = \frac{A}{8\pi Dgr^2 h^2} = \frac{1.62 \times 10^{-25}}{r^2 h^2} \quad \dots 7)$$

where the value of  $D$  for ash was taken to be  $2500 \text{ kg m}^{-3}$  and when  $h < 1.5 \times 10^{-8} \text{ m}$ . The corresponding ratio ( $F_r'$ ) of the retarded van der Waals forces ( $F'$ ) to the gravitational force is given by:

$$\frac{F'}{F_g} = F_r' = \frac{2B}{Dgr^2 h^3} = \frac{8.15 \times 10^{-34}}{r^2 h^3} \quad \dots 8)$$

where  $h > 1.5 \times 10^{-8} \text{ m}$ .

Fig. 5 shows a comparison of van der Waals and the gravitational forces on small ash particles as these approach a collecting surface. Plots A and B indicate that the sub-micron sized particles are readily held on a surface by van der Waals forces. The capture of small particles of ash on boiler tubes is further enhanced by surface irregularities of oxidized metal (19). Also, it has been suggested that an electrostatic attraction force enhance the transport and retention of sub-micron sized particles on steel probes inserted in the flue gas of coal fired boilers (7,20). A layer of electrically precipitated deposit of ash can have a cohesive strength between 5 and 40 times higher than that formed by sedimentation because particles in an electric field have permanent dipole characteristics which lead to these being orientated to form a cohesive layer of ash (21). It appears therefore that the combined effects of van der Waals and electrostatic forces of attraction, and surface irregularities are sufficient to hold the sub-micron diameter particles on the surface of boiler tubes for the subsequent liquid phase adhesion, and chemical and mechanical bond formation.

#### ADHESION BY SURFACE TENSION FORCE

The formation of strong adhesive bonds of enamel coatings and glass/metal seals on heating requires the presence of a liquid phase (22,23,24). The role of the liquid film is to provide the initial adhesion of solid particles as a result of surface tension. The work of adhesion ( $W_a$ ) is given by:

$$W_a = \pi + \gamma (1 + \cos \theta) \quad \dots 9)$$

where  $\gamma$  is the surface tension of the liquid, and  $\theta$  is the contact angle at the solid/liquid interface. With perfect wetting, i.e. when  $\theta$  equals zero,  $W_a$  has the highest value:

$$W_a = \pi + 2\gamma \quad \dots 10)$$

The work of cohesion of a liquid ( $W_c$ ) is given by:

$$W_c = 2\gamma \quad \dots 11)$$

With wetting liquids, therefore,  $W_a$  can be higher than  $W_c$  and failure will take place within the liquid layer, whereas with non-wetting liquids the rupture occurs at the solid/liquid interface.

Alkali-metal sulphates frequently constitute a liquid phase in ash deposits, and the molten sulphates readily wet and spread on the surface of boiler tubes. In a reducing atmosphere and when in contact with carbon, sulphates are reduced to sulphides which wet and spread on any surface. The coefficient of surface tension of sulphates is fairly high,  $0.20 \text{ N m}^{-1}$  for  $\text{Na}_2\text{SO}_4$  and  $0.14 \text{ N m}^{-1}$  for  $\text{K}_2\text{SO}_4$  near their respective melting point temperatures (25,26). Thus work of cohesion of molten sulphate layer in boiler deposit is between  $0.3$  and  $0.4 \text{ N m}^{-1}$  and the work of adhesion is higher because of a low contact angle at the sulphate/tube surface interface. It is therefore to be expected and it is observed in practice that when the deposit is removed, e.g. by sootblowing, there remains a film of sulphate adhering to boiler tubes. The surface tension of coal ash slag has been measured previously by the sessile drop method (27) and a typical value was  $0.3 \text{ N m}^{-1}$ . It is about twice that of sulphates and thus the work of adhesion (Equation 9) and the cohesive bond strength are corresponding higher at the slag/solid interface.

Only a small amount of liquid, about a hundred molecule thick layer, is sufficient for the adhesion contact of sub-micron diameter particles (28). In the case of a volatile liquid, the equilibrium thickness of the film, and thus the adhesion, varies with partial pressure of the vapour in the surrounding atmosphere. When evaporation from a liquid film occurs, as a result of increased temperature, the adhesion first rises to a maximum value due to the meniscus effect but it breaks down as the film thickness is reduced to molecular dimensions. However, before the break-down of the surface tension chemical and mechanical bonds may develop between the deposited ash and boiler tube surface.

#### MECHANICAL AND CHEMICAL BONDING

Ash deposits on boiler tubes can be keyed to the surface of metal oxide by mechanical and chemical bonds. Mechanical bonding is enhanced by extending surface at the interface as shown in Fig. 6a. Boiler tubes are not polished and thus have an extended surface that is further increased by oxidation and chemical reactions between the oxide layer and ash deposits. It is therefore evident that a comparatively rough surface of boiler tubes constitute an anchorage for keying ash deposits to the heat exchange elements.

Dietzel (29) and Staley (30) have proposed that the chemical reactions at a enamel/metal interface can be considered in terms of electrolytic cells set up between the metals of different electro-chemical potential. It has been suggested that cobalt or nickel precipitated in the enamel when in contact with steel surface, forms short-circuited local cells in which iron is the anode. The current flows from iron through the melt to cobalt and back to iron. The result is that iron goes into solution, the surface becomes roughened, and the enamel material anchors itself into the cavities as shown in Fig. 6b.

The galvanic reactions will take place at a much faster rate in the low viscosity phase of sulphates in boiler deposit than that in highly viscous silicate glass. However, rapid reactions at the tube surface/deposit interface may not be necessary or appropriate for development of a strong bond between the ash deposit and boiler tubes. In metal/glass seal and metal/enamel coating technology, the adhesive bonds formed on heating have to be completed in a few hours, whereas those in boiler deposits can form over a period of days or weeks. The adhesive bond between the metal surface and a silicate material can be high when there is a gradual rather than abrupt change in the glass phase composition near the interface (31).

When the ash deposit is brought in intimate contact with the surface of boiler tubes either by the action of surface tension or by the galvanic reactions, the controlling parameter in mechanical bonding is the strength of the glassy phase at the narrowest cross sectional area of contact cavities (Fig. 6b). The annealed glass may have a tensile strength of around  $50 \text{ MN m}^{-2}$  giving a maximum bond strength of  $35 \text{ MN m}^{-2}$ . However, the glass at the interface may be stronger or weaker depending on whether the conditions in the keying cavities increase or decrease local flaws and resultant stresses.

Chemical bonds, covalent or ionic as shown in Fig. 6c and d, at the metal oxide/deposit surface are potentially strong with theoretical values over  $10^9 \text{ N m}^{-2}$ . It is, however, impossible to estimate the number of sites and the size of contact areas at the interface where the chemical bonds may be effective. In any case, the cohesive strength of the deposit matrix is the limiting factor since it is lower than that of chemical bonds by several orders of magnitude. In practice, this means that when a strongly adhering deposit is subjected to a destructive force, e.g. sootblower jet, failure occurs within the deposit matrix and there remains a residual layer of ash material firmly bonded to the tube surface.

#### ADHESION OF ASH DEPOSITS ON FERRITIC AND AUSTENITIC STEELS

The adhesion bond strength of soda glass on a metal substrate has been determined by heating a glass disc sandwiched between two metal discs in a vertical furnace (32). The technique has been adopted for measuring the strength of the adhesive bond developed when a boiler deposit was sandwiched between two discs of ferritic or austenitic steels (33). The deposit material was taken immediately after boiler shut-down from the superheater tubes of a pulverized coal fired boiler fuelled with a mixture of East Midlands, UK coals. The flue gas temperature in the superheater prior to boiler shut-down was about 1300 K and the tube metal temperature was 850 K. The deposit material consisted of 30 per cent of alkali-metal sulphates in weight ratio of 2 to 1 of  $\text{Na}_2\text{SO}_4$  to  $\text{K}_2\text{SO}_4$ , the remainder being silicate ash. A layer of deposit, 3 mm thick, was sandwiched between two metal discs, 20 mm in diameter, made of boiler tube steels and then heated in a vertical furnace. After a time interval lasting from one to 25 days the bond was ruptured by applying a tensile force without prior cooling.

The results in Fig. 7 show that the strength of adhesive bond between the ferritic steel sample and boiler deposit increased exponentially with

temperature in the range of 775 to 900 K. Similar results were obtained by Moza et al. (34) who used a droplet technique to measure the adhesive bond of coal ash slag on a ferritic steel target in the temperature range of 700 to 950 K.

The results plotted in Fig. 8 shows that the strength of adhesive bond of ash deposit on both the ferritic and austenitic steels increased approximately linearly with time at 900 K. However, the bond strength of deposit on the austenitic steel (Type 18Cr13NiNb) was significantly lower than that between the deposit and 9Cr-ferritic steel. The latter resulted from the thermal and chemical compatibility of the steel oxide layer and deposit material (35). Table 1 shows approximate values of the coefficient of thermal expansion of the ferritic and austenitic steels, some oxides and silicate materials (36).

Table 1: Coefficient of Thermal Expansion of Boiler Tube Steels, Oxides and Silicates

Material	Thermal Expansion, $\frac{\Delta m}{m} K^{-1}$
<u>Steels</u>	
Mild Steel and Ferritic Steels	11 to 12 $\times 10^{-6}$
Austenitic Steels	16 to 18 $\times 10^{-6}$
<u>Oxides</u>	
Tube Metal Oxides (Fe <sub>3</sub> O <sub>4</sub> , Cr <sub>2</sub> O <sub>3</sub> , NiO)	8 to 10 $\times 10^{-6}$
<u>Deposit Constituents</u>	
Glassy Material	6 to 9 $\times 10^{-6}$
Quartz (Crystalline)	5 to 8 $\times 10^{-6}$
Silicates in Fired Brick	7 to 8 $\times 10^{-6}$

The data in Table 1 show that the coefficient of thermal expansion of mild steel and ferritic steels is not greatly different from that of their oxides and the ash deposit constituents. It is therefore evident that there is no gross incompatibility in the thermal expansion characteristics and strongly bonded ash deposits once formed on mild steel tubes are not easily dislodged on thermal cycling.

In contrast, the thermal expansion of austenitic steel is significantly higher than that of the oxides and deposit material. In the absence of boiler deposit, the oxide material in the form of thin layer is able to absorb thermal stresses and the adhesive layer remains intact on cooling. However, it appears that the oxide layer is unable to absorb thermal stresses in a similar manner when contaminated and constrained by bonded ash deposits. It is therefore a usual occurrence that ash deposits peel off the austenitic steel tubes on cooling whereas the deposit formed on ferritic steels under the same conditions remain firmly attached to the tubes.

King et al. (22) have suggested that in order to obtain good adherence of enamel coatings on metals, the enamel material at the interface must become saturated with the metal oxide, e.g. FeO of ferritic steels. Coal ash deposit on boiler tubes contains between 5 and 25 per cent iron oxide (Fig. 1) and thus the layer at the tube/deposit interface becomes saturated with FeO. The chromium and nickel contents of ash deposit are low and thus the same chemical compatibility stage is not reached at the austenitic steel/deposit interface.

The adhesive bond between boiler ash deposit and the surface of ferritic steels can attain exceptionally high strengths. This was found on examining the deposits formed on different steel specimens tested in an experimental superheater loop. Favourable conditions for the formation of firmly bonded deposits were as follows:

- (a) The iron oxide content of coal was above 20 per cent expressed as  $\text{Fe}_2\text{O}_3$  giving an iron saturated layer of deposit on the tube specimens.
- (b) The ash collecting surface was a 5 per cent chromium ferritic steel which formed an oxide layer strongly adhering to metal for a firm anchorage of deposits.
- (c) The tube metal temperature was high, 950 K, which enhanced the formation of strong adhesive bond. The flue gas temperature at that position was approximately 1250 K.
- (d) The ferritic test piece in the experimental loop was sheltered from direct action of sootblower. Weak turbulence caused by the jet removed some of the unsintered silica ash leaving iron rich deposit firmly bonded to the tube. The iron rich deposit had grown in thickness to about 20 mm after nine months, and cohesive strength of the deposit material increased towards the surface of tube metal. The microscopic examination showed that there was no marked interface boundary between the ash deposit and metal oxide.

#### FORMATION OF LAYER STRUCTURE DEPOSITS AND SLAG MASSES

The coal ash deposits on boiler tubes have frequently a separate zone structure with a sulphate rich layer up to 2 mm thick under the matrix of sintered ash (35). The outer layer is porous and it constitutes a pathway for the enrichment of alkali-metals in the deposit layer next to tube surface. The diffusable species may be sulphate, chloride, oxide or hydroxide, but the thermodynamic data (8) and the results of deposition measurements in coal fired boilers (Fig. 3) suggest that sodium and potassium sulphates are the principal vapour species which diffuse through a porous matrix of silicate ash deposit.

The relative amounts of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  which diffuse through the sintered matrix of silicate ash depend on the temperature gradient across the deposit layer, vapour pressure of the species and thermodynamic stability of the sulphates in the presence of silicates. Potassium sulphate has a higher temperature stability limit when compared with that of sodium sulphate and as a result  $\text{K}_2\text{SO}_4$  can be preferentially transported to the surface of cooled boiler tubes when there is a steep temperature gradient across the ash deposit. The  $\text{K}_2\text{SO}_4$  rich phase, when molten, can cause severe corrosion of tube metal.

The corrosion product, a mixture of oxide, sulphide at the metal interface and sulphate outside, has a weak adhesive bond to the metal surface and cannot support large deposit masses. It is therefore unusual to find excessive amounts of sintered ash deposits and fused slag in the exact localities where severe high temperature corrosion occurs. Conversely, a strongly adhering matrix

of sintered ash deposit in the absence of sulphate, sulphide or chloride phases is not markedly corrosive.

The build-up of boiler tube deposits is a continuously changing process as depicted in Fig. 9. When the deposit material reaches a thickness of 2 to 3 mm (Fig. 9a) the separate sulphate and silicate phases occur (Fig. 9b). Subsequently, the sulphate layer disappears in the middle section (Fig. 9c) allowing a strong bond to be established between the sintered ash deposit and ferritic steel boiler tubes. This is the "classical" mode of formation of superheater tube deposit when the metal temperature is in the range of 750 to 900 K. Above 950 K the layer structured deposits are less likely to occur and a strong adhesive bond is rapidly formed between the silicate ash deposits and the high temperature tube surface.

A notable feature of slag formed in pulverized coal fired boiler is its variable gas hole porosity. Burning coal particles are encapsulated in the deposit layer and generate CO and CO<sub>2</sub> inside the silicate material (27) resulting in a highly porous slag. The density of slag will increase when the encapsulated coal particles are consumed and gas bubbles have escaped.

It has been observed that new boilers have an "immunity" period lasting weeks or months before severe slag build-up occurs. This is partly due to the fact that during the commissioning period the boiler rarely reaches full load output. However, it may also be partly due to a slow rate of formation of the interface layer on boiler tubes which is able to have a strong adhesive bond to rapidly forming ash slag and thus able to support large masses of deposit.

## CONCLUSIONS

### Initial Deposit

The initial deposit material on cooled tubes in coal fired boilers consists largely of flame vitrified silicate ash, iron oxide, and calcium and alkali-metal sulphates. Trace amounts of chloride will also deposit and under reducing conditions some iron and calcium sulphides can be present.

### Phase Separation

Most coals leave an ash residue which is pyrochemically acidic, and the alkali-metals and calcium are distributed in the silicate and sulphate phases under oxidizing conditions. The fused silicates and molten sulphates are immiscible and separate into two phases. The phase separation enhances the adhesion of ash to boiler tubes and leads to the formation of layer structured deposits.

### Initial Particle Adhesion

Initially the small particles of ash, below 1  $\mu\text{m}$  in diameter are held at the surface of boiler tubes by the van der Waals and electrostatic attraction forces. Subsequently a film of molten sulphate may form at the tube surface/deposit interface and only a small amount of liquid, about one hundred molecules thick is sufficient for bonding.

### Strong Adhesive Bond of Deposits on Ferritic Steels

Strong adhesive bonds can form between the oxidized surface of ferritic steels and iron rich ash because of the composition and thermal expansion compatibility of the metal oxide and silicate ash deposit. The adhesive bond strength increases exponentially with temperature of the target surface in the

range of 750 to 950 K. The bond strength can reach high values, that is, higher than the cohesive strength of sintered ash deposits at temperatures above 850 K.

#### Weak Adhesive Bond of Deposits on Austenitic Steels

The adhesive bond between the austenitic steel surface and ash deposit is relatively weak as a result of the composition and thermal incompatibility of the steel oxide and the silicate material. The temperature fluctuations on changeable boiler load conditions can cause sufficiently high thermal stresses for deposit to skid off the austenitic steel tubes.

#### Boiler Tube/Ash Deposit Interface

The boiler tube/ash deposit interface layer which can support large masses of slag formed in the combustion chamber takes several months to develop. Thus the full extent of boiler slagging may not become evident during the commissioning period of new boiler plant.

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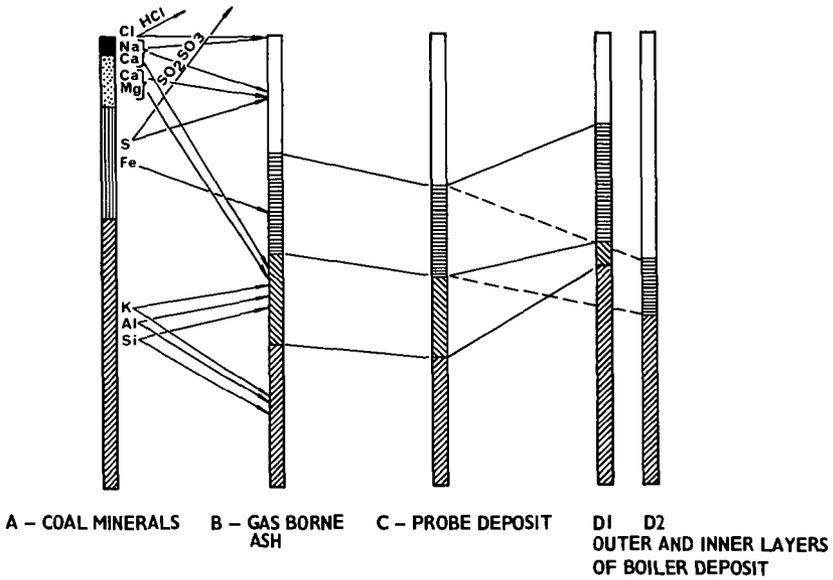
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**FIG. 1**    ASH COMPOSITION CHANGES ON ROUTE FROM MINERAL MATTER TO BOILER TUBE DEPOSITS

- |  |   |  |
|--|---|--|
|  IN SOLUBLE SILICATES |  SOLUBLE SILICATES |  |
|  PYRITES              |  IRON OXIDES       |  CARBONATES |
|  CHLORIDES            |  SULPHATES         |  |

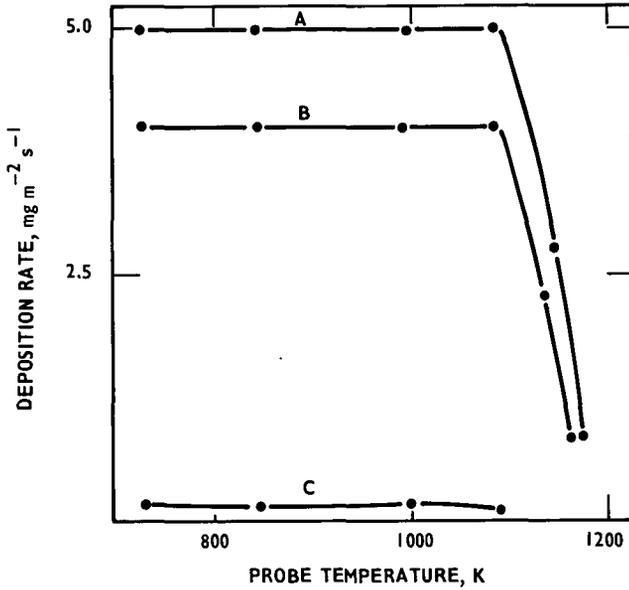
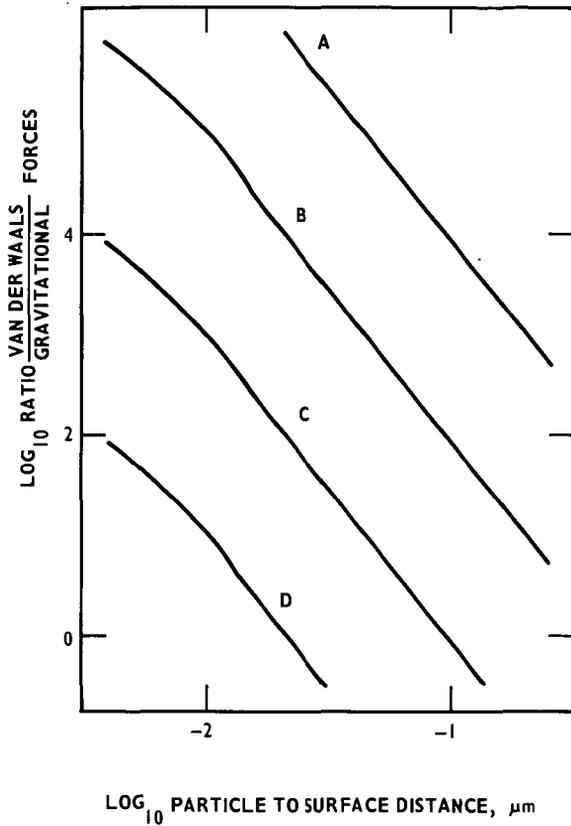


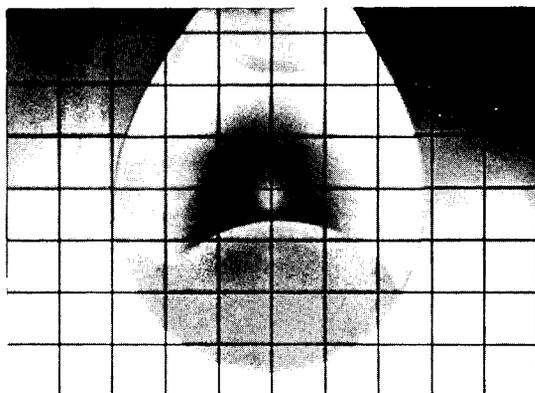
FIG. 2 DEPOSITION OF SULPHATE AND CHLORIDE IN CYCLONE FIRED BOILER - 0.28 PER CENT CHLORINE IN COAL

A -  $\text{Na}_2\text{SO}_4$  B -  $\text{K}_2\text{SO}_4$  C - NaCl



**FIG. 5** COMPARISON OF VAN DER WAALS AND GRAVITATIONAL FORCES ON ASH PARTICLES NEAR COLLECTING SURFACES

PARTICLE DIAMETER, μm  
 A - 0.01; B - 0.1; C - 1.0; D - 10.0



TWO PHASES AT 1575K

FIG. 3  $2K_2SO_4 - K_2O - 2.1 SiO_2$  DROPLET IN HEATING MICROSCOPE (0.5 mm GRID)

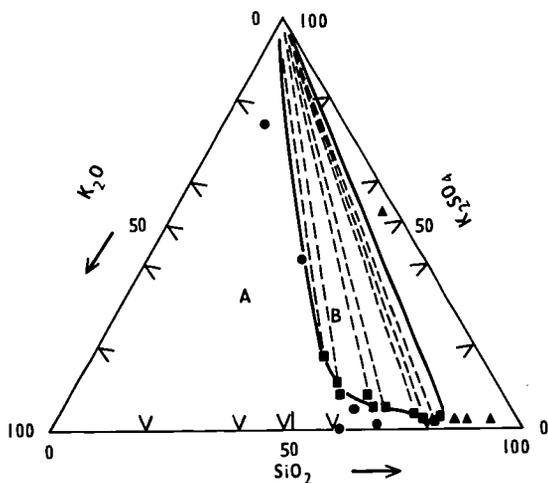
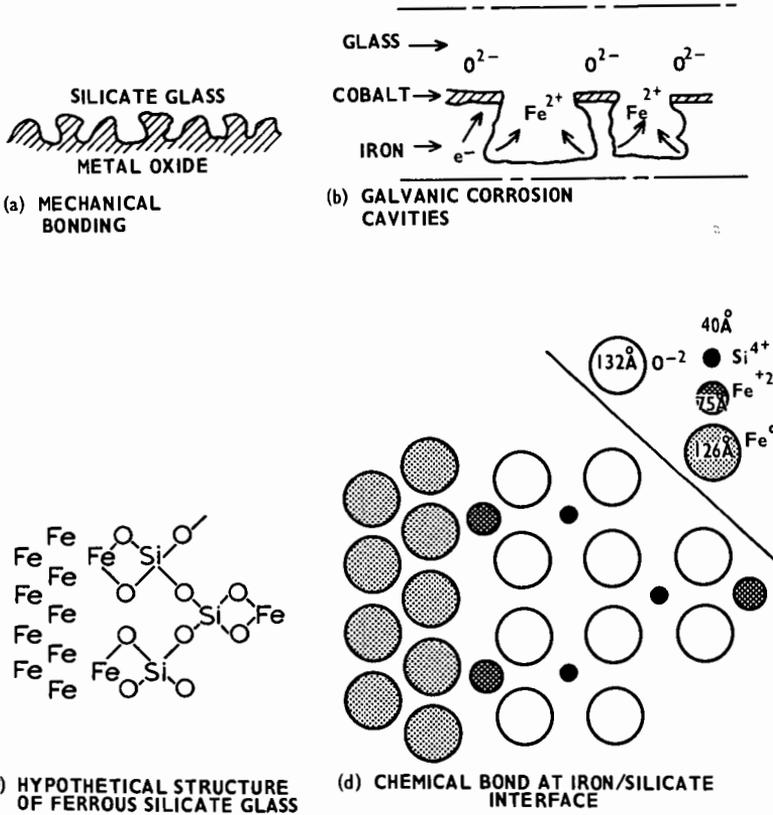


FIG. 4 MISCIBILITY GAP IN  $K_2SO_4 - K_2O - SiO_2$  SYSTEM AT 1575 K  
 A, SINGLE PHASE B, TWO PHASES C, LIQUID + SOLID  $SiO_2$



**FIG. 6 SCHEMATIC REPRESENTATION OF MECHANICAL AND CHEMICAL BONDS AT BOILER TUBE/ASH DEPOSIT INTERFACE**

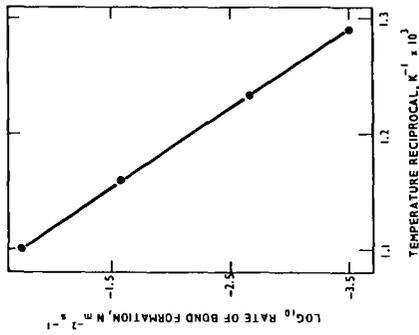


FIG. 7 THE EFFECT OF TEMPERATURE ON ASH DEPOSIT/FERRITIC STEEL BOND

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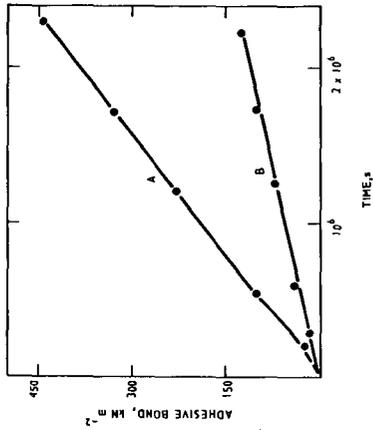


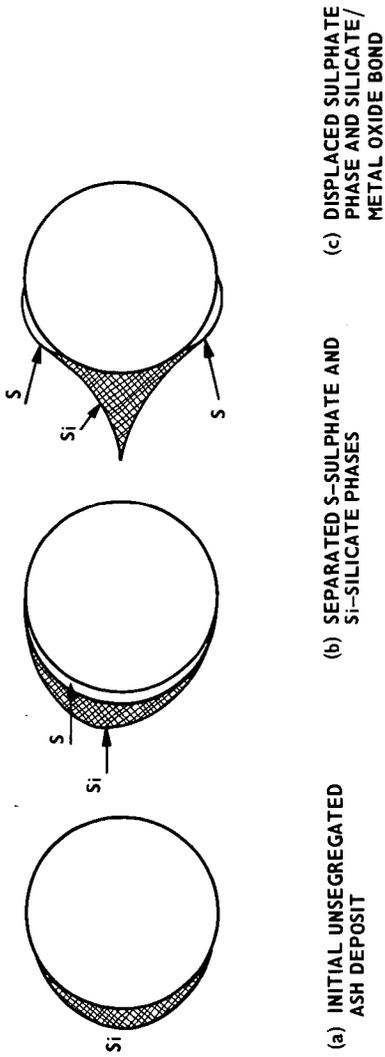
FIG. 8 BOND STRENGTH BETWEEN ASH DEPOSIT AND BOILER TUBE STEELS AT 900 K

A - FERRITIC STEEL

B - AUSTENITIC STEELS

(R)

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**FIG. 9** SEQUENTIAL STAGES IN THE FORMATION OF LAYER-STRUCTURED AND FIRMLY  
ADHERING SUPERHEATER DEPOSIT