INFLUENCE OF SEGREGATED MINERAL MATTER IN COAL ON SLAGGING

R. W. Bryers

Foster Wheeler Development Corporation
12 Peach Tree Hill Road
Livingston, New Jersey 07039

INTRODUCTION

The mineral content of any given rank of coal is a key factor in sizing and designing a steam generator or reactor. The mineral content becomes even more important as the premium solid fuels are consumed, leaving reserves with continual increasing mineral concentrations and lower quality ash. The problem of dealing with lower quality ash in coal is compounded by the increase in size of steam generators and refinements imposed by economic constraints. Empirical indices, based on coal ash chemistry and ASTM ash fusion temperatures or viscosity, are presently used to rank coals according to the fireside behavior of the mineral matter. Unfortunately, the indices are only marginally satisfactory, as they do not relate to operating or design parameters and frequently are based on a coal ash chemistry quite different from that deposited on the furnace wall. Frequently, different coals with identical ash chemistry produce decidedly different slagging conditions in steam generators of identical design operated in the same mode. Variations in composition of the slag, when compared with the coal ash, suggest specific minerals are being selectively deposited on furnace walls depending upon their specific gravity, size, composition, and physicochemical properties. It is quite apparent there is a need for a better understanding of the impact of mineral composition, its size, and its association with other minerals and carbonaceous matter on fireside deposits.

MINERAL MATTER IN COAL

Minerals occurring in coal may be classified into five main groups. These include shale, clay, sulfur, and carbonates. The fifth group includes accessory minerals such as quartz and minor constituents like the feldspars (1).

Shale, usually the result of the consolidation of mud, silt, and clay, consists of many minerals including illite and muscovite--these are forms of mica. Kaolinite is the most common clay material (1).

The sulfur minerals include pyrites with some marcasite. Marcasite has the same chemical composition as pyrites but a different mineralogical structure. Sulfur is also present as organic matter and occasionally as sulfate. The latter usually occurs in weathered coal such as in outcrops. The amount of sulfate sulfur in coal is generally less than 0.01 percent.

Generally, 60 percent of the sulfur in coal is pyritic, particularly when the sulfur concentration is low. At higher concentrations it may run as high as 70 to 90 percent. Pyrite occurs in coal in discrete particles in a wide variety of shapes and sizes. The principal forms are (1-6):

- Rounded masses called sulfur balls or nodules an inch or more in size.
- Lens-shaped masses which are thought to be flattened sulfur balls.
- Vertical, inclined veins or fissures filled with pyrite ranging in

thickness from thin flakes up to several inches thick.

- Small, discontinuous veinlets of pyrite, a number of which sometimes radiate from a common center.

- Small particles, <72μ, or veinlets disseminated in the coal. Microscopic pyrite occurs in five basic morphology types: (a) framboids, (b) isolated euhedral crystals, (c) nonspherical aggregates of euhedral cyrstals, (d) irregular shapes, and (e) fractured fillings (7).

All coals contain some of the third and fifth forms of pyrite, and some coals contain all five of the principal forms (6,8,9).

The carbonates are mainly calcite, dolomite, or siderite. The occurrence of calcite is frequently bimodal. Some calcite occurs as inherent ash, while other calcite appears as thin layers in cleats and fissures. Iron can be present in small quantities as hematite, ankorite, and in some of the clay minerals such as illite. In addition to the more common minerals, silica is present sometimes as sand particles or quartz. The alkalies are sometimes found as chlorides or as sulfates but probably most often as feldspars, typically orthoclase and albite. In the case of lignites, unlike bituminous and subbituminous, sodium is not present as a mineral but is probably distributed throughout the lignite as the sodium salt of a hydroxyl group or a carboxylic acid group in humic acid. Calcium, like sodium, is bound organically to humic acid. Therefore, it too is uniformly distributed in the sample.

The term, "mineral matter," usually applies to all inorganic, noncarbonaceous material in the coal and includes those inorganic elements which may occur in organic combination. Physically, the inorganic matter can be divided into two groups--inherent mineral matter and extraneous mineral matter. Inherent mineral matter originates as part of the growing plant life from which coal was formed. Under the circumstances, it has a uniform distribution within the coal. Inherent mineral matter seldom exceeds 2 - 3 percent of the coal (10).

Extraneous mineral matter generally consists of large bits and pieces of inorganic material typical of the surrounding geology. In some cases the extraneous matter is so finely divided and uniformly dispersed within the coal it behaves as inherent mineral matter. Coal preparation can separate some of the extraneous ash from the coal substance, but it seldom removes any of the inherent mineral matter.

The physical differences between inherent and extraneous ash are important not only to those interested in cleaning coal but also to those concerned with the fireside behavior of coal ash. Inherent material is so intimately mixed with coal that its thermal history is linked to the combustion of the coal particle in which it is contained. Therefore, it will most likely reach a temperature in excess of the gas in the immediate surroundings. The close proximity of each species with every other species permits chemical reaction and physical changes to occur so rapidly that the subsequent ash particles formed will behave as a single material whose composition is defined by the mixture of minerals contained within the coal particle. The atmosphere under which the individual transformations take place will, no doubt, approach a reducing environment. Figure 1 illustrates a model of the coal and mineral matter as fed to the combustor and the fate of the minerals after combustion (11).

Extraneous materials can behave as discrete mineral particles comprised of a single species or a multiplicity of species. As already indicated, a portion of this material may be so finely divided it can behave as inherent mineral matter.

During combustion the larger particles respond individually to the rising temperature of the environment. In the absence of carbon or other exothermic reactants, the particle should always be somewhat less than the local gas temperature. However, the particles may be subjected to either reducing or oxidizing conditions. As each particle rises in temperature, it loses water of hydration, evolves gas, becomes oxidized or reduced, and eventually sinters or melts, depending on its particular composition or temperature level.

It is evident, then, that there can be a great difference in the final state of each particle, depending upon its composition and whether it is inherent or extraneous ash. Figure 2 summarizes the phase transformations which pure mineral matter commonly found in coal undergoes during heating (12,13,14). Since this data was developed primarily by mineralogists performing differential thermal analysis under air at slow heating rates, it must be used only as a guideline for predicting the thermal behavior of minerals in coal. Thermal shocking these minerals in the presence of carbon and other mineral forms at very high temperatures, no doubt, will alter some of these transformations and may defer others until postcombustion deposition on heat transfer surfaces.

Clays and Shale

The melting temperatures of most pure minerals are in the vicinity of or greatly exceed the maximum flame temperature encountered during combustion. Therefore, the fused spheroidal fly ash, generated from the mineral matter in coal, primarily forms as the result of the fluxing action between pure minerals contained within each particle. Illite and biotite appear to be an exception. Both minerals contain small concentrations of iron and potassium and form a glassy phase at 950°C and 1100°C, respectively. Depending upon its fluidity, this glassy phase could be responsible for surface deformation at a relatively low temperature and provide the necessary sticking potential to prevent reentrainment upon contacting heat transfer surfaces. Low temperature ash of a gravity fraction containing illite was heated in a thermal analyzer under air to 600 and 1000°C, respectively, and compared to the low temperature ash of a gravity fraction void of illite. The scanning electron photomicrographs, appearing in Figure 3, indicate the minerals containing illite did, indeed, show signs of the formation of a melt.

Quartz

The inherent silica retained in the char as quartz or silica released from kaolinite and illite at low temperatures (i.e., 950°C) is partially reduced to silica monoxide. Unlike silica which boils at 2230°C, silica monoxide melts at 1420°C and boils at 2600°C (15). The vapor pressure of silicon is low--in the range of temperatures experienced during combustion. Honig reports values ranging from 0.01m Hg at 1157°C to 1m Hg pressure at 1852°C (15,16). The presence of other mineral matter and carbonaceous material appears to alter vapor pressure substantially. When a mixture of alumina silicate and graphite was heated, the volatilization of silicon monoxide began at about 1150°C and reached a maximum at 1400°C. Mackowsky reports that volatilization of silicon monoxide starts at about 1649°C in the presence of carbonates and clays and reaches a maximum at 1704°C (17). In the presence of pyrite or metallic iron, volatilization begins at about 1560°C and continues at a rapid rate as the temperature rises until practically all the silica in the mineral is volatilized. Sarofin has shown that about 1.5 to 2.0 percent of the ASTM ash in bituminous coals volatilize (18). Approximately 35 - 40 percent of the volatilized material was silica. The next largest component was iron. Extraneous quartz appears to be relatively innocuous unless contaminated by Fe_2O_3, CaO, or K_2O.

Pyrites

The decomposition of pyrite has been examined by numerous investigators under oxidizing, neutral, and reducing environments. TGA, rather than DTA, has been used by most investigators. Acquisition of representative data is difficult, as the decomposition process is complex and sensitive to many variables including the chemical composition of pyrites, its grain size, its origin, the presence of adventitious impurities, the composition of the local environment, and diffusion rates through sulfated layers. Under oxidizing conditions it is believed that pyrites decompose directly to an iron oxide and SO_2 or SO_3 or iron sulfate and SO_2, depending upon the final temperature level. Under reducing conditions pyrrhotite and either carbon or hydrogen sulfide form. Complete reduction results in elemental iron and carbon disulfide. There is also a possibility that pyrrhotite may form under oxidizing conditions as an intermediate step in the presence of sufficient adventitious carbon. Pure pyrites ignite at about 500°C in the thermal analyzer at 20°C/min and burn out by 550°C in a single-step process, as shown in Figure 5. Pure pyrites do ignite as readily as bituminous coal; however, the burnout time is comparable. Although pyrrhotite ignites readily, it requires as much time as anthracite to complete combustion. Pyrites containing small quantities of adventitious carbon, as might be found in the -1.80 +2.85 gravity fraction, appear to form pyrrhotite, deferring burnout until 800°F. Within the combustor the problem is compounded by the fact that pyrite particles do not shrink during the combustion process as do coal particles, and hence, their burnout time is extended. The burnout time of particles in excess of 40μ appears to exceed the residence time available in most combustors.

TGA reveals decomposition rates but tells little about the physical state during the combustion process. Phase diagrams for the Fe-S-O and FeS-FeO system, representing transitory states at the particle surface, imply the formation of a temporary melt at low temperatures. SEM photomicrographs, appearing in Figure 5, of pure pyrites heated to 600°C, 800°C, and 1000°C under reducing conditions clearly reveal the formation of a melt at temperatures as low as 600°C. Large particles of partially-spent pyrites, which may be molten on contact with the heat transfer surface, complete the oxidation process in situ, forming a solid fused deposit with a very high melting temperature.

An examination of the thermal behavior of the mineral matter in coal indicates the mineral origin of the elements found in coal ash and their juxtaposition with regard to each other, as well as other mineral forms, and determines their physical fate during combustion. As indicated in Figure 1, the physical state (i.e., vapor or solid) and the size of solidified ash will determine the mode and rates of migration to the heat transfer surface. The physical state at the tube surface will depend upon the local surface temperature and the composition of the particulate depositing. In the case of pyrites residence time and environment conditions may also play a significant role.

CHARACTERIZATION OF MINERALS IN COAL

The fireside behavior of mineral matter in coal has been investigated by characterizing the mineral content of several bituminous coals, using size and gravity fractionation analysis of pulverized coal and then firing the coal in a vertically fired combustor. High sulfur coals containing pyrites of varying size and varying association with carbonaceous and other mineral forms were selected for examination. A comparison was also made with western subbituminous coals to assess the impact of potassium in the mineral illite on furnace slagging.

Each coal was analyzed for proximate, ultimate, ash chemistry, and ash fusion temperatures to permit evaluation using conventional data. The pulverized coal samples were then divided into four sizes representing equal weights (i.e., +105μ, -105μ +74μ, -74μ +44μ, and -44μ). Each size fraction was separated into four weight classes, thereby, partitioning the coal into groups dominated by coal, nonpyritic mineral matter, and pyrites. The partitioned coal was analyzed for ash chemistry, ash fusion temperature, combustion profile, and mineral content.

The analytical data is summarized in Figure 6. The enclosed data points represent the composite analysis. The open data points represent the fractionated species. Ash softening temperatures and percent basic constituents were selected as the variables to characterize the coal, as they appear most frequently in the indices used to express the slagging or fouling potential of the fuel. It is quite evident the combustor is exposed to ash with a wide range of chemical compositions and melting temperatures not adequately identified by a composite coal analysis. The data indicates slagging was most severe with coals having the highest melting temperature and demonstrating the greatest degree of separation of ash from coal and pyrites from other mineral matter. The two coals with the lowest composite ash softening, having the highest slagging index by conventional evaluation, caused the least slagging. Liberation of mineral matter from these two coals was also the lowest.

The data was replotted on fusibility diagrams, appearing in Figure 7, typifying the coal with the greatest partitioning of mineral matter and highest degree of slagging and the coal with the least liberation of mineral matter and degree of slagging. The fusibility diagram illustrates the size and weighted contribution of each ash specie. It also shows the degree of liberation of nonpyritic and pyritic mineral matter. By washing the worst coal at 1.80 sp. gr. and 14M x 0, thereby minimizing extraneous ash as well as total sulfur, the degree of slagging of the Upper Freeport coal was greatly reduced.

COMBUSTION TESTING

Deposits were removed from various locations in the combustor after firing each coal for ≅14 - 16 hours. Samples were removed from slagging probes at 398 - 510°C, fouling probes at 510 - 537°C, and refractory surfaces at 537 - 1204°C and examined using the scanning electron microscope and energy dispersive x-ray. Fly ash samples were also examined for carbon loss, surface morphology, and chemical composition.

The deposits forming on the slagging probes were initiated by a thin layer of powdery fly ash, <8μ in size, enriched with small quantities of potassium. Beads of slag formed on top of this thin layer when the surface temperature approached the initial deformation temperature of the deposit. Growth progressed with the formation of rivulets from which a continuous phase of molten slag formed. Deposits forming on the refractory surface represent an advanced stage of slag due to the higher surface temperatures which could only be achieved on the cooler probes after the initial dust layer formed. The composite ash chemistry and ash fusion temperatures of the slag resemble that of the heaviest gravity fraction (i.e., >1.80 sp. gr.) in most cases. Macrophotographs of the deposit formation on the furnace probes subjected to axial symmetric flow at low gas velocities (5 - 6 ft/s), illustrated in Figure 8, show that the initial layer of dust, upon which further slagging depends, formed only when firing coals whose ash contained more than 1 percent potassium. Continued deposit growth resulting in serious slagging is dependent upon the total pyrites liberated from the coal.

SEM microphotographs and EDAX scans of the cross section and outer surface of the slag deposit, illustrated in Figure 9, indicate the chemistry of the deposit is not uniform. The bulk of the fused material is rich in silica, low in iron, and virtually depleted of potassium. The outermost layers, no more than 2 to 3μ thick, are very rich in iron and frequently also rich in calcium. On occasions, the outer surface is covered with small particulate several microns in diameter or undissolved cubic or octahedral crystals whose origin is pyrites. Similar formations have been observed in full-scale operation. The evidence indicates deposits form under axial symmetric flow conditions in the furnace by the fluxing action at the heat transfer surface of small particles, <8μ in diameter, of decidedly different chemical composition and mineral source. Migration of the fly ash to the surface is by means of eddy diffusion, thermophoresis, or Brownian motion.

Sintered deposits form at the furnace exit at lower gas temperatures and in zones subject to rapid changes in direction. The deposit is composed of spheroidal particles <40μ bound together by a molten substance. In those cases where substantial quantities of coarse pyrites are liberated from the pulverized coal, the spheroids are nearly pure Fe_2O_3, as shown in Figure 10. The matrix contained silica, alumina, iron, and potassium and has an initial deformation temperature of 1000°C, as determined by differential thermal analysis. The heavier pure iron spheroids deposit as a result of inertial impact. The mineral source of the molten phase is most likely illite.

Deposits also form on the leading edge of the first row of tubes in the convection pass when firing coals which liberate pure, coarse pyrites. These tubes are subjected to high gas velocities and have moderate to high collection efficiencies for particles between 40 and 100μ. The deposits are nearly pure Fe_2O_3. They are hard and fused despite being at gas temperatures below their initial deformation temperature. No doubt, the final stages of decomposition of the pyrites takes place at the tube surface.

CONCLUSIONS

The formation of fireside deposits in furnaces depends on the composition, size, and association of mineral matter liberated from the coal. Selective deposition of specific mineral species depends on their size, thermal behavior, the local gas temperatures, and their mode of transport to the surface. Consequently, the composition of the sintered deposit or molten slag may vary with time at a given location and will most probably vary throughout the combustor, depending on local temperatures and fluidynamics. The composition of the slag may be substantially different from the composite coal ash, depending upon its heterogeneity. Illite is a likely candidate as the mineral most responsible for initiating deposits. The molten phases are frequently part of the $FeO-SiO_2$ or $FeO-CaO-SiO_2$ system and depend on the interaction of quartz, calcite, or pyrites at the heat transfer surface. Liberated pyrite crystals and small particles are primary candidates for slag formation subjected to parallel flow regimes at low velocities. Coarse pyrites can be selectively deposited and solely responsible for deposit formation on surfaces subjected to flue gas impingement at high velocities.

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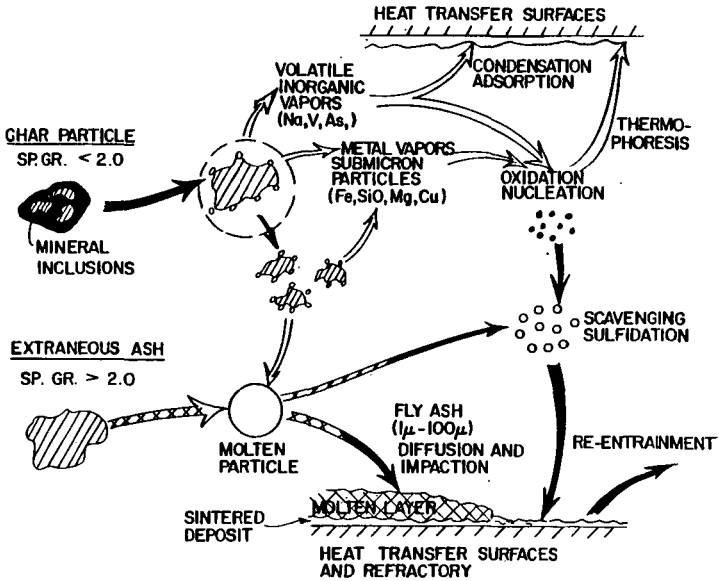


Figure 1 Fate of Mineral Matter in Coal During Combustion, as Proposed by Dr. Sarofin

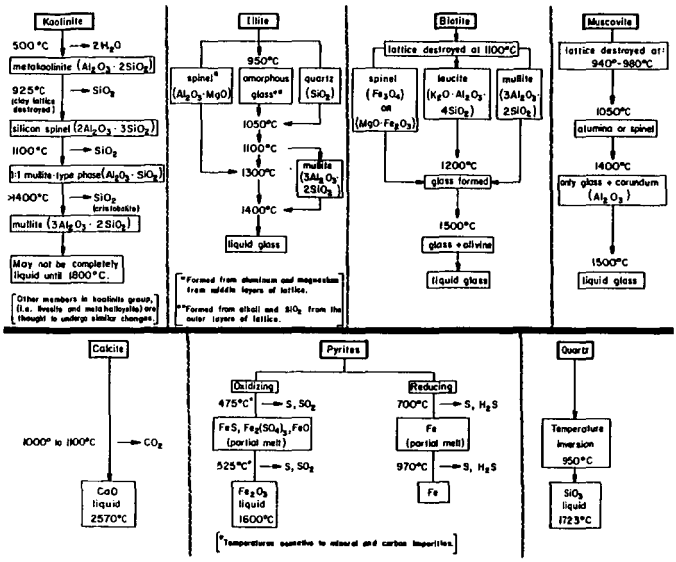
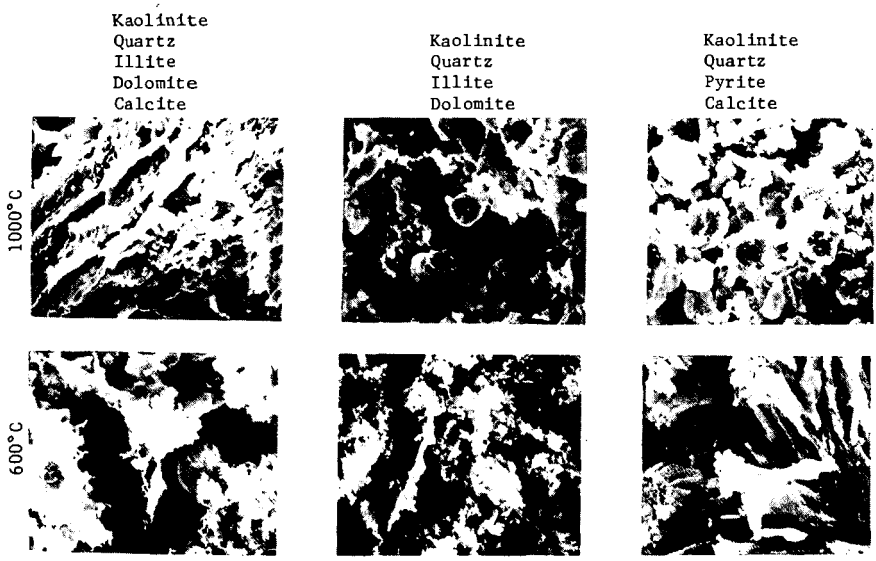


Figure 2 Phase Transformation of Some Mineral Matter Commonly Found in Coal



Mag. 3000X

Figure 3 SEM Photomicrographs Showing the Impact of Illite on the Thermal Behavior of Low Temperature Ash

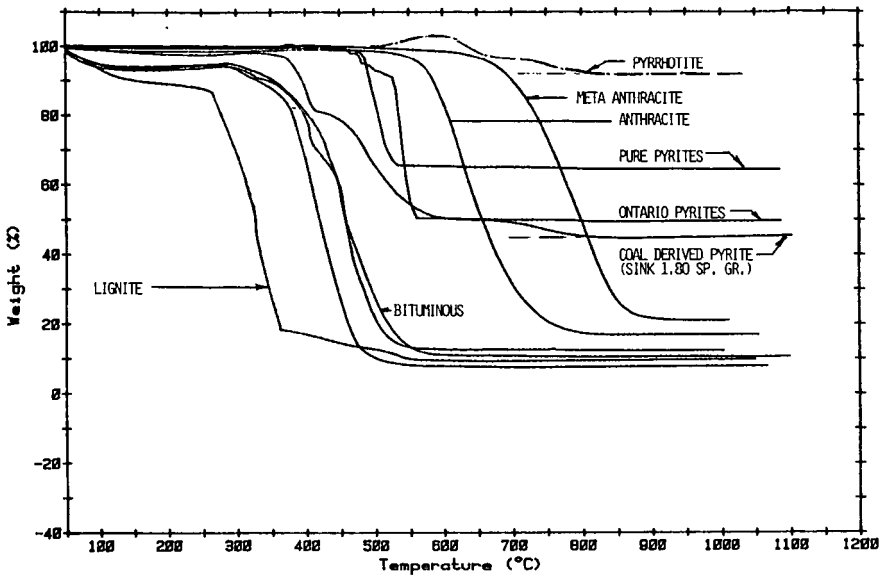


Figure 4 TGA Thermograms Comparing the Decomposition of Various Grades of Pyrites with Various Ranks of Coal

Mag. 3000X

600°C 800°C 1000°C

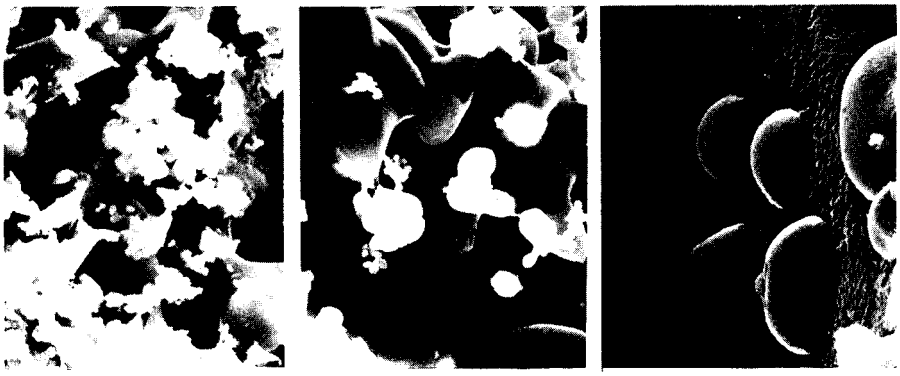


Figure 5 Pure Pyrites Heated Under Reducing Conditions to 600, 800, and 1000°C

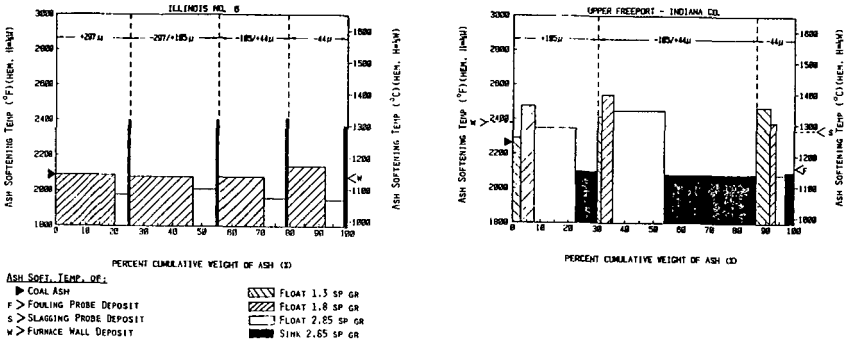


Figure 7 Fusibility Diagrams

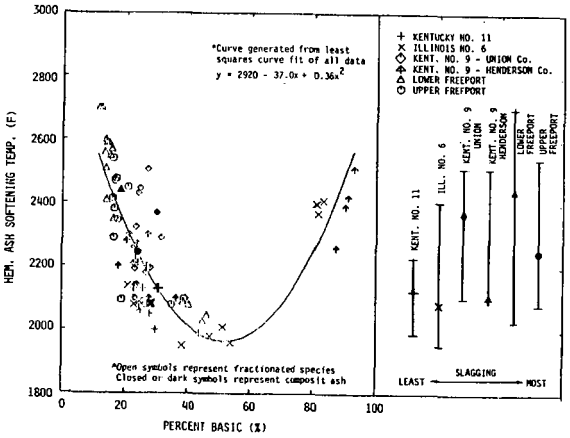


Figure 6 Ash Softening Temperature Vs. Percent Basic for Composite and Fractionated Coal Species

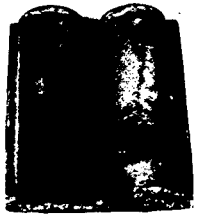
Ash Soften. Temp. (Red) and % Ash	% Liberated Fe_2O_3 in Coal			%Kin Ash	Ash Soften. Temp. (Red) and % Ash
2130°F 14.9	Kentucky No. 11 0.225			Western Fuel 1 0.2	2165°F 6.7
2080°F 9.4	Illinois No. 6 0.159			Western Fuel 2 1.0	2252°F 16.67
2443°F 16.4	Lower Freeport 1.56			Western Fuel 3 1.2	2232°F 25.73
2245°F 23.5	Upper Freeport 1.67			Lower Freeport 2.5	2443°F 16.4

Figure 8 Slagging on Furnace Probes after 14 - 16 Hours Operations

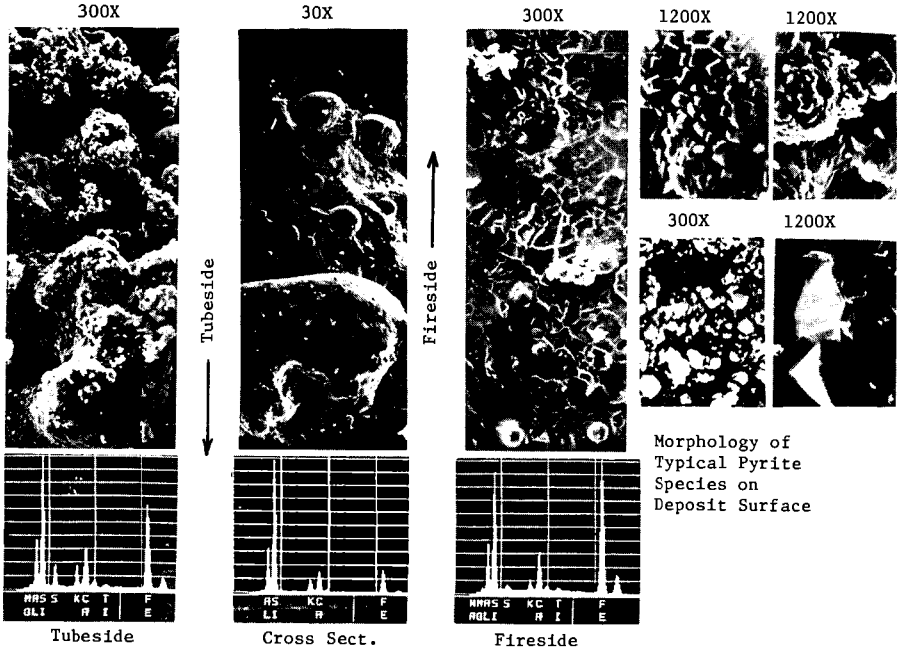


Figure 9 Slag Formation on Furnace Slag Probe

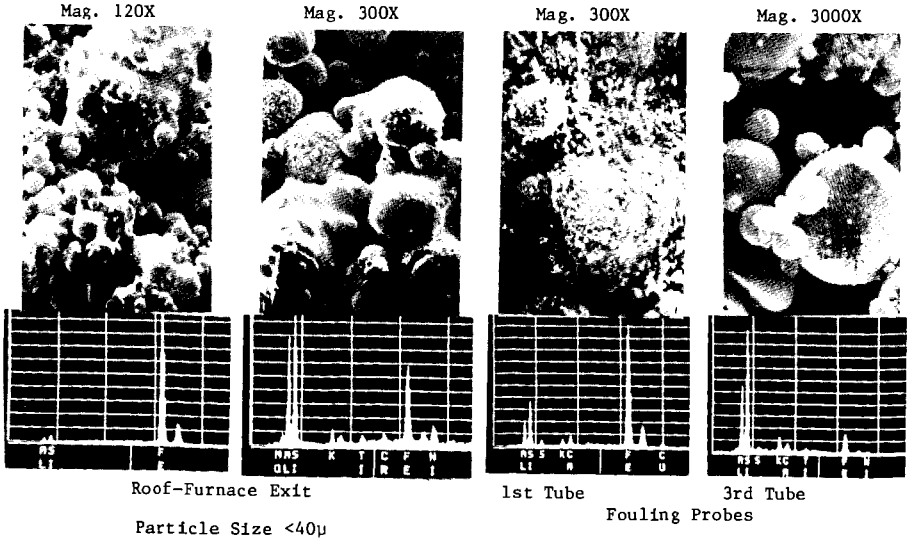


Figure 10 Iron-Rich Sintered Deposits Formed on Furnace Roof and 1st Tube of Convection Pass Probes by Coarse Pyrites