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STUDY OF THE MINERAL MATTER DISTRIBUTION IN PULVERIZED
FUEL COALS WITH RESPECT TO SLAG DEPOSIT FORMATION IN
BOILER FURNACES. PHASE 1

Final Report for Period April 1, 1976—June 30, 1980

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July 1980
Date Published

Work Performed Under Contract No. AS22-76ET10560

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U. S. DEPARTMENT OF ENERGY

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**STUDY OF THE MINERAL MATTER DISTRIBUTION
IN PULVERIZED FUEL COALS WITH RESPECT
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Phase 1

Final Report for the Period

1st April 1976 - 30th June, 1980

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Date Published - July 1980

**PREPARED FOR
THE UNITED STATES DEPARTMENT
OF ENERGY**

Under Contract No. EF-76-S-01-2316

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ABSTRACT

The work reported here is aimed at understanding the initiation of upper wall slag deposits in pulverized coal fired utility boilers, and characterizing pulverized coals for the mineral elements of significance. A scanning electron microscope with X-ray fluorescence capability, under computer control, has been used to analyze individual coal particles for the elements Si, Al, Ca, Fe and S. The required software for these analyses has been developed, as has suitable sample preparation techniques. The results show many different types of particles to exist in pulverized coal, some of which are likely to be bad-acting in terms of slagging.

A test has been developed to study the sticking of melted pellets of ash or mineral matter dropped onto a metal substrate held at a controlled temperature. It was found that for a given drop composition and substrate material there is a substrate temperature below which the drop will not adhere. At higher substrate temperatures the strength of adhesion increases logarithmically. Sticking appears to be a function of the oxidation of the surface or of alkalies deposited on the surface. If the drop composition is such that material absorbed from the substrate fluxes the drop-substrate interface, then the apparent contact angle is reduced and sticking is enhanced, and vice-versa.

A small-scale pulverized coal furnace designed to give a uniform temperature-time history for each particle was reconstructed and tested. Water-cooled probes were found to give the most accurate control of initial probe temperature. Deposits initiate on the probe in a few minutes, and the fall of probe temperature can be used to indicate the growth of deposit. Systematic investigation of the particles initiating the deposit have not yet been performed.

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OBJECTIVE AND SCOPE OF WORK

It is proposed to study the correlation of the mineral matter of pulverized coal (p.c.) fuel with slag deposit formation in electric utility boilers. Using the computerized scanning electron microscope (SEM) technique developed at Penn State it is possible to estimate the mineral matter content of powdered coals on a particle-by-particle basis. The properties of a droplet of slag formed from a particle of coal will depend on the mineral matter in that particular particle, not the mean mineral content of the whole coal. The p.c.'s studied will be supplied from power plants having various degrees of difficulty with slagging, a complete particle property matrix determined for each sample, and the results examined to determine the bad acting constituents.

The coals will also be studied in a one-dimensional (plane flame, plug flow) laboratory p.c. furnace, which passes all coal particles through the same temperature-time history, to determine the slagging behavior of the coal under controllable standard conditions.

Four important novel ideas are embodied in the proposal. First, that it is no longer necessary to determine the mean ash composition of coal, since the new technique enables different types of particles in the p.c. to be identified. Second, the slag initiation may be caused by a relatively minor number of ash spheres origination from individual coal-mineral matter particles. Third, that the controlled one-dimensional furnace offers a solution to the problem of constructing a meaningful laboratory test for slagging propensity. Fourth, the studies of the wetting and contact angle of slag droplets on surfaces may be much more informative than simple melting behavior, since deposit initiation involved sticking of a droplet to the furnace wall.

There are five major tasks involved as follows.

Task 1 (Sample Collection): the collection of coal samples and boiler plant history from operating power plant. This is expected to be an ongoing task, leading to the collection of as many as 20 samples. However, in the first phase a minimum of four different pulverized coal samples from commercial electric utility plants (including the Keystone and Conemaugh Plants of the Pennsylvania Electric Company) will be collected for study by visits to the plant sites by the Penn State investigators. Sample selection criteria will be based on radically different behavior of the coals on boiler firing. A minimum of 20 lbs ($< 1/2''$) and as much as several hundred lbs of sample will be collected, along with information on sample

history. The pulverized coal samples will be separated into sized fractions by dry sieving or wet sieving, depending on analytical agreement of these methods. Float-and-sink techniques for separation will also be considered.

Task 2 (Sample Analysis): for each of the raw pulverized coal samples collected, the following analytical data will be obtained:

A. Elemental analyses of the important mineral elements will be obtained using the techniques developed at Penn State University by Suhr (atomic absorption spectroscopy and standard flame photometry).

B. Conventional coal analyses tests (including ultimate and proximate analyses, Btu heating value, ash fusion temperature, free swelling index, and sulfur modes (sulfate, pyritic, organic) will be obtained.

C. Semi-quantitative and quantitative mineralogical analyses will be performed on the residues from electronic low-temperature ashing (as developed by O'Gorman and Walker of Penn State University), using the analytical methods of x-ray diffraction and infrared absorption spectroscopy.

D. Complete petrographic analyses will be performed on polished specimens of the coals.

The above described analytical data for the raw feed coal samples will be obtained in the Penn State in-house analytical laboratories under ERDA Contract No. 3(49-18)-2030.

Task 3 (Particle Analysis for Microscale Studies on Fusion Effects): the pulverized coal samples will be subjected to matrix analysis by computerized SEM (Scanning Electron Microscopy), using the SEM in the microprobe mode, to determine the interelement relationships for a number of elements in the sample on a particle-by-particle characterization basis. This will establish a matrix of particle properties for distinguishing between "trouble-free" and "trouble-causing" coals. Intercomparisons of these CESEMI (Computer Evaluation of Scanning Electron Microscope Images) matrices for the different coals will be made to identify "bad-actor" mineral or element components. Thus the CESEMI technique supplies unique information more useful than the conventional mean-composition of coal. The size and shape distribution of each particle type will be obtained from analyses of a statistically significant number of particles. CESEMI analysis will yield the degree of association of mineral components of coal on a particle-by-particle basis.

Task 4 (Laboratory Tests on Slag Deposition): the pulverized coal samples will be subjected to tests, as necessary, in various furnaces available at the Penn State University Combustion Laboratories. The

available test furnaces include: (a) an electrically heated "isothermal" tube furnace which will give a controlled heating history up to about 1000°C (~ 1800°F) and with enough flexibility and control of operating conditions to simulate plant experience and (b) a specially designed "one-dimensional" flame furnace in which the flow is "once-through" (no back-mixing).

Task 5 (Wetting and Contact Angle): a high temperature glow-bar furnace (with well-controlled temperature and gas atmospheres) and a 250 watt Hg lamp viewing system will be constructed to carry out tests of the enameling characteristics (wetting and contact angle of slag droplets) of different mineral constituents. These will include tests on melting of coal ashes, synthetic mixtures of mineral matter, and combinations of the two.

SUMMARY

The preliminary investigations of the research showed that the software of the existing CESEMI (Computer Evaluation of Scanning Electron Microscope Images) system at Penn State was unsuitable for pulverized coals and that the camphor-naphthalene dispersing technique did not properly disperse coals. A method was developed using dispersion in water with three reagents, followed by freeze-drying on a slide, which gave excellent dispersion of coal and mineral particles. However, x-ray fluorescence measurements on pure mineral particles using the SEM in the microprobe mode showed too high deviations from the correct values. This was due to the "geometric" effect with particles of irregular shape. Mineral particles mounted in a matrix and polished to a smooth plane surface gave good results. The technique did not work on coals, for a number of reasons, and a developmental program was undertaken.

An analysis of the general principles of measurement and corrections of SEM/x-ray fluorescence data was performed. The electron beam, under computer control, moves across a test surface, leading to emitted secondary electron and electron back-scatter signals which are detected and analyzed. The electron back-scatter signals are used to distinguish one material from another, so that at any x,y coordinate on the surface a report of on-a-particle (off background) or off-a-particle (on background) is made. The beam is brought to rest on sampling points within the particle, and the characteristic x-ray fluorescence generated from each point is detected and analyzed in a multichannel analyzer. This beam excites a volume about 5 μm diameter in the particle.

It was concluded that certain features must be included in order to get correct results. First, the coal particles must be mounted in a heavy-metal-containing resin which gives clear contrast between the coal and the resin. Second, the electron back-scatter image must be inverted to make the coal appear brighter than the background. Third, because a mineral occlusion in the particle will then appear as background (thus leading the beam to believe it has left the particle) it is necessary to define the perimeter of the particle before scanning across the exposed particle section. Fourth, due to time delays in the electronics and magnets, the x,y coordinates calculated from the time of movement of the beam shift slightly depending on the previous history of the beam, so that the edge of a particle appears fuzzy or grey to a perimeter tracing method; this effect must be allowed for. Fifth, the selection of sampling points within the particle must give sample volumes wholly within the particle, not overlapping into the matrix. Sixth, existing ZAF programs for correcting the characteristic x-ray counts of one element for the presence of other elements were too time-consuming to be suitable for the analysis of thousands of particles.

These features were incorporated into the existing hardware system as follows. After a number of trials of various resins and heavy metal organic additions, a mounting medium was developed which contained barium. The operating program was modified to invert the back-scatter signal. A program was written to trace and store the x,y coordinates of the perimeter of an exposed particle section. This program included the logic to make the beam march across a fuzzy edge until the interior was reached, back out until the matrix was reached, move up or down, then progress in this fashion around the edge of particles of complex shape. A program was written to deduce the center coordinates of circles of 8 μm diameter fitted within the perimeter of a particle. The sampling points for x-ray excitation were chosen from these center coordinates, thus ensuring sampling over the particle but not too close to the edge. The test slides were made from particles sized into ranges using micromesh sieves, e.g. 10x20 μm . The mean diameter of the detected exposed cross-section was determined by a line integral of the perimeter x,y coordinates. If the diameter was smaller than the original particle size range, it was assumed that the section might be only a minor fragment of the particle, without an 8 μm depth, and the particle was not examined further. If the section were of the right size it was assumed to be a section through the bulk of the particle, thus being a proper choice for test.

Finally, an abbreviated ZAF procedure designed specifically for this task was written "from scratch." It was written for the elements Ca, Si, Al, Fe and S, with all other elements being considered as carbon and oxygen. It involves a first estimate of the particle composition based on the comparison of the counts of characteristic x-rays for these elements from the particle compared to those from pure minerals. This first estimate is used in the correction procedure to get second estimates, and so on. A maximum of 4 iterations was used to give reasonable accuracy consistent with time demands. The steps of perimeter tracing, choice of sampling centers, excitation and counting, and ZAF corrections were programmed in an interrupt mode to obtain the maximum overlap of data sampling and computation, to reduce the total sampling-computer time to a minimum.

The method has been applied to mixtures of pure alumina and calcite particles and shown to give approximately the correct values for Al and Ca. The data from coals is analyzed by splitting the particles into various types depending on the amount and composition of the inorganic elements in the particle. Type I contains less than 5% mineral matter, Types II and III contain FeS_2 and Fe_2O_3 respectively, Types IV and V are the remaining particles with estimated inorganic compositions indicating a liquidus temperature below 1550°C (sticky) or above 1550°C (non-sticky) respectively. Types II and III were further subdivided depending on the % of Fe in the ash, with compositions with more than 50% Fe_2O_3 or 25% FeS_2 being likely to be sticky. A comparison of the results on Rosebud and Comanche coals showed that Rosebud had much higher percentages of Type IV and high Fe sub-types II and III than Comanche, and would therefore be expected to be a bad slagger. This was in agreement with the full-scale experience with these coals, even though most other indices of slagging predicted Comanche to be worse than Rosebud. Keystone coal had a much higher proportion of high Fe sub-types II and III and is hence predicted to cause iron-rich slag deposits.

The preliminary work to investigate the contact angle of the molten ash drops on a substrate showed that coal ash does not wet carbon but does wet platinum, and reacts with alumina. Addition of iron to ash caused an increase in wetting. Quantitative reproducibility of the results was poor and attempts to study molten ash in contact with a colder metal substrate did not succeed. Consequently, an entirely new apparatus was developed: the "sticking test apparatus". This consisted of an upper system of opposed flames and a lower system in which a test substrate is maintained at a controlled temperature. The test consists of melting a pellet of ash or mineral mixture with methane-oxygen flames until it melts to form a drop which falls onto the test substrate below. High speed photography showed that the interface between the drop and the metal solidifies within 1 to 3 milliseconds, with a zone of solidification moving up through the drop until it is all solidified in about 40 milliseconds. The apparent contact angle formed by the solidified drop on the substrate was measured, as was the force required to shear off the drop. It was found that if the substrate temperature was below a critical temperature T_s the drop would not adhere. As the substrate temperature was higher, a drop would stick with greater adhesion force, with the strength of adhesion increasing approximately logarithmically with temperature.

Detailed investigations of the drop-substrate interface using an SEM and electron microprobe gave the following conclusions.

For an ash drop to stick strongly to a colder metal surface it is necessary that the interfacial region between the two should be liquid in its initial stages of formation. The sticking temperature is drastically modified by a coating of sodium chloride on the substrate. The oxide layer on a mild steel substrate plays a crucial role in the sticking of ash drops. It appears that ash drops adhere to the oxide layer and, upon shear, parts of this oxide layer are broken off the substrate. This indicates that adherence between the oxide layer and ash drop is stronger than the adherence of oxide layer to the metal. Ash drops show poor sticking on stainless steel substrates up to 600°C when compared to oxidized mild steel.

The interaction between the molten ash drop and colder oxidized metal surface seems to be of a chemical nature. This interaction takes place in a very short time, probably in milliseconds, and extends over a region of a few micrometers. The sticking of the ash drop is greatly enhanced when the metal surface is coated with sodium chloride probably because sodium chloride can flux the interface of the ash drop at the surface. The sticking is also enhanced by the presence of NaCl or FeS₂ in the drop itself. Further, not all of the sodium chloride or sulfur are driven out of the drop. In the case of sodium chloride, it seems that sodium is able to react within the ash drops during melting. Pyrite drops adhere very strongly to the oxidized metal substrates and the results indicated some pitting or penetration of the metal. Further, pyrite drops stick to substrates in the form of pyrrhotite (Fe_{0.995}S) drops.

The apparent contact angle and sticking temperature-adhesion behavior can only be reproduced if the substrate surface is prepared in a standard manner, although the adhesion force versus temperature appears to be less sensitive to surface state than the contact angle. The oxide film which grows on mild steel affects the contact angle, giving increased apparent wetting at lower temperatures for any condition which thickens the film, such as higher preoxidation temperatures, longer preoxidation times, and

substrate temperatures high enough for the film to form as the substrate is brought up to temperature. In general, increased wetting correlates with reduced sticking temperature, and sometimes with increased adhesion force. Creation of a more porous oxide layer decreased contact angle and increases adhesion strength. There is substantial evidence for movement of iron and fluxes into the drop.

It can be hypothesized that the spreading of a drop on the surface until it solidifies is a function of three major factors: (i) the surface tension between the drop and the surface, dependent on the chemical nature of the surface and the drop; (ii) the viscosity of the glass at the interface, dependent on the drop composition and how rapidly the interface chills and (iii) the physical state of the surface, that is, micro-capillary action. It seems likely that the presence of a layer of iron oxide will enhance spreading on all of these accounts, since iron oxide is more compatible with the inorganic oxides of the glass than bare metal, a layer of iron oxide reduces the rate of heat conduction away from the interface and keeps the glass less viscous for a longer time, and the oxide layer is microporous. The adhesion force also can be postulated to depend on three factors: (i) the contact area as indicated by the apparent contact angle; (ii) the chemical bonding between glass and substrate; and (iii) the mechanical keying produced by penetration and solidification of glass into micropores on the substrate surface. Again, it is likely that these three factors are, in general, enhanced by the presence of oxide films.

It appears that in order for a strong bond to form between the drop and the oxide film on the substrate it is necessary to form an interfacial region consisting of both iron oxide and slag. The formation of this region is assisted by long times of contact of liquid slag with the substrate, since reactions will be very slow in a solid-solid system at the relatively low substrate temperatures of 600°C and less. A heat transfer calculation indicated that higher substrate temperature and lower liquidus temperatures greatly increase the time to completely solidify a 2 μ m thick interface. A slag composition which has a low liquidus temperature, and in which the liquidus temperature decreases as it picks up iron, will tend to stick more readily to the substrate.

The apparent contact angle measured in this type of test is probably not an equilibrium contact angle because of the short times of liquid-solid contact, but represents the wetting, spreading and flattening of a drop during the time of freezing of the contact. Low substrate temperatures tend to give high contact angles because they reduce the time of solidification. Low apparent contact angle does indicate more wetting and a wider area of contact, therefore additional bond strength. In addition, the bond may be partially formed by penetration of slag into micropores in the substrate surface. In this case, penetration is also aided by low surface tension, low viscosity and long solidification times.

Any compound on the surface which fluxes the interfacial region as it is absorbed into the substrate-drop interface will tend to aid sticking by lowering the liquidus temperature and possibly reducing the surface tension and viscosity. Any compound which raises the liquidus temperature, increases the surface tension and viscosity or makes the drop interface chemically incompatible with the substrate will tend to prevent sticking. In addition, it is possible that a compound which promotes rapid crystallization in the interfacial region might also greatly reduce the bond strength.

Preliminary results from the reconstructed laboratory-scale pulverized coal furnace showed that deposit initiation on a substrate at controlled temperature could be studied by water-cooled probes. In agreement with the sticking test, deposits initiated more rapidly at higher substrate temperatures. Deposits from Keystone coal were iron-rich. Deposits from Illinois #6 coal indicated that the sticking particles had mainly Al, Si, and Ca, thus would be of Type IV.

SECTION 1. INTRODUCTION AND SUMMARY OF EARLY WORK (Interim Reports FE-2316-1 to FE-2316-9)

1.1. Introduction

This project was originally started with three Principal Investigators, Professors E. G. White, R. H. Essenhig and L. G. Austin. Due to resignation from the University, Professors White and Essenhig only participated in the early stages of the work reported here. Because of the consequent added burden on Professor Austin, and because the experimental techniques originally envisaged were radically modified in the light of experience, the original contract period of April 1976 to March 1979 was extended at no extra cost to June 1980.

This final report consists of a brief summary of the early, primarily exploratory, phases of the research, plus more detailed exposition of the final techniques and results. To prevent excessive rewriting, the later sections are in the form of chapters from student theses (where the descriptions are too lengthy for publication) or of technical publications arising from the contract research.

1.2. Task 1 - Collection of Samples

Discussions with Mr. James Tice of the Pennsylvania Electric Company led to several coals being considered for study, as being bad slagging coals. In addition to the type of coal, the following parameters were considered by operators to be relevant to slagging:

- (i) coal sources
- (ii) coal grindability
- (iii) particle size distribution of the pulverized coal
- (iv) furnace design
- (v) furnace heat loading
- (vi) high S content
- (vii) high moisture content

Items (ii), (iii), and (vii) may be related in-as-much as a low grindability and high moisture content can lead to a particle size distribution which is coarser than usual. Larger particles tend to burn out more slowly, leading perhaps to hotter particles reaching the upper regions of the furnace. Also, large particles tend to be thrown against the wall, whereas fine particles sweep forward in the gas stream leaving the furnace.

It is difficult to get truly comparative data from different plants because of these influences. The inadequacy of basing the choice on existing slagging indices is shown in Table 1, which is based on special slagging tests at the Keystone Power Station (Pa). Although the Canterbury coal was low in S, had a high ash fusion, and a low slagging index, it gave slag build-up problems in the furnace. Another complicating factor was tests where the coal normally fired at Keystone was cleaned from 19.2% ash, 2.26% S to 9.3% ash, 1.53% S. The cleaned coal also gave slag problems,

TABLE 1
COAL ANALYSES FOR SLAGGING TESTS

Keystone Generating Station
Special Coal Analyses - 1969

Sample Description	Composite R+P Prod. Emily-Jane-Margaret Mines Sampled May 7-12, 1969	Canterbury Station Sample	Washed Coal R+P Production 1.7F 3"x28M
Sample Identification No.		KDL No. 2510C	
Sample Taken At	Keystone		
Sampled By	R+P Coal Co.		
Date Sampled	May 7-12, 1969		
Proximate:	Dry Basis	As Received	Dry Basis
Moisture		0.7	
VM		30.2	
FC		53.5	
Ash	19.23	15.6	9.29
Sulfur	2.26	1.4	1.53
Btu/lb as fired		12,630	
Btu/lb dry	12,339		14,014
Btu/lb dry, ash-free			
Ash Fusion Temp., F			
ID (Reducing Basis)	2,230	2,700 ⁺	2,195
ST (H-W)	2,470	2,700 ⁺	2,585
FT	2,595	2,700 ⁺	2,700
ID (Oxidizing Basis)			
ST			
FT			
Ash Analysis:			
SiO ₂	51.26	50.8	45.86
Al ₂ O ₃	24.45	30.2	29.87
Fe ₂ O ₃	15.95	9.1	15.02
TiO ₂	1.43	1.0	1.47
CaO	1.76	1.3	2.39
MgO	0.47	1.1	0.71
Na ₂ O	0.28	0.3	0.36
K ₂ O	2.34	3.3	2.57
P ₂ O ₅		0.4	
SO ₃		0.7	
Chlorine as %, Dry Coal			
Grindability			
Ash Viscosity			
Indices:			
Base/Acid Ratio	0.27	0.18	0.27
Lb Ash/10 ⁶ Btu Fired		12.4	
Slagging Index	1.61	0.252	1.41
Fouling Index	0.71	0.054	1.79

ID: Initial Deformation
ST: Softening Temperature
FT: Fusion Temperature

and it was found that the composition of the ash was relatively unchanged by the cleaning. If anything, the slag problem was worse for the cleaned coal, with a one-inch thick layer of slag forming over substantial areas of the walls.

A sample of 100 kg of pulverized coal from the Keystone plant, consisting of Upper Freeport E seam coal was selected as one test coal. In addition 6 drums of unpulverized coal taken at the time corresponding to feeding to the pulverizers were also obtained. Four unpulverized coals (50 kg lots) were obtained from Combustion Engineering, Inc., Hartford, Conn. These were Upper Freeport (Pa); Illinois #6; Wyoming (School) Sub-bituminous and a Texas (Wilcox) lignite. One of these coals, Illinois #6 was pulverized in a pilot-scale Babcock E-type mill by the Kennedy Van Saun-DOE test facility (Danville, Pa). This type of mill is used for preparing pulverized coal for boiler firing. Rosebud and Comanche coals were also obtained from Combustion Engineering, in small quantities suitable for laboratory tests. Combustion Engineering has pilot-scale and full-scale data on the relative behavior of these six coals.

1.3. Task 2 - Sample Analysis

The coal samples have been analyzed by the conventional proximate and ultimate analyses, and have also been analyzed for petrographic constituents, inorganic constituents of ASTM ash, and mineralogical analysis of LTA ash. Sampling procedures from unpulverized samples were in accordance with ASTM standards D2234 and D2013.

For petrographic analysis, a sample was dried at 55°C in an oven for 12 hours. The coal sample was mixed with Paraplex P43, an acrylate, to which a cobalt accelerator had been added. The contents were transferred to a sample bottle (1" dia., 3" height) coated with a releasing agent and the mixture allowed to harden for 24 hours. Two coal pellets were obtained after breaking the bottle, which was cut into two halves. Each pellet was cast with epoxy (plus hardener) resin in a steel mold. After the epoxy had hardened, the block containing the coal pellet was removed. Each pellet was approximately 1" in dia. and 1-1/2" in height. The surface of the pellet was ground on a revolving wheel covered with Carborundum Company number 400 and 600 silicon carbide grit. The pellet surface was further polished on a revolving steel wheel covered with a polishing cloth coated with hydrated alumina (0.3 μ size) and water. Final polishing was carried out using a polishing cloth impregnated with alumina (0.05 μ size) set in a rotating wheel. The polished surface was cleaned in a ultrasonic bath then washed with distilled water and air dried. The specimen was then ready for petrographic analysis. The maceral analysis was carried out at the Penn State Mineral Constitution Laboratory using the point count method on a Leitz model BME microscope.

Inorganic elements were determined by quantitative spectrometric analysis at the Penn State Mineral Constitution Laboratory.

Mineralogical analysis was also performed at these laboratories using the techniques developed by Painter et al⁽¹⁾ at Penn State. The technique

consists of computer Fourier transform analysis of IR data from the sample.

The results of these analyses are reported in sections 2.5.1 to 2.5.7 at positions relevant to the results of the contract studies.

1.4. Task 3 - Particle Analysis of Microscale Studies on Fusion Effects

The existing software attached to the computerized scanning electron microscope was designed to recognize mineral inclusions in a polished matrix. It was found to be inappropriate for studying coal particles because the beam did not recognize coal particles distinct from the mounting resin. The technique was therefore used to study coal particles dispersed on a carbon base. The camphor-naphthalene technique suggested by White^(2,3) was found to be unsuitable for coal. Consequently, a more conventional technique based on dispersing the particles in water was used.

The dispersing agent used was a mixture of ionic and surfactive agents, to give a dispersing solution of 0.2% NPX Tergiton, 0.1% Calgon and 0.1% Daxad 11 KLS, weight % of coal. This mixture was deduced from the work of Datta⁽⁴⁾, and was employed in the sequence: coal + Calgon solution is stirred, NPX-Tergiton added, shaken and the Daxad added finally. The suspension is then treated for one minute in an ultrasonic bath prior to preparing the slide. Calgon is a dispersing agent for minerals, NPX-Tergiton is a wetting agent for coal and Daxad is a dispersant for coal.

With the help of a pipette a drop (approx. 0.1 gms) of the dispersed sample is transferred to a cleaned carbon planchet surface. The drop is covered with a slide cover and the slide is cooled (by liquid nitrogen) to freeze the sample. The glass slide cover is twisted off using a razor blade, leaving a frozen thin layer of the sample on the carbon planchet. The carbon planchet is then put in a vacuum system, where the ice is sublimed off without melting the sample. After the ice has sublimed off, the slide is viewed under a microscope to check the absence of agglomerates. If agglomerates are present, a fresh slide is prepared. Before analyzing the slide under SEM, carbon is deposited on it using the conventional technique of a carbon arc in vacuum.

This dispersing and freeze-drying technique was found to give excellent dispersion of even the smallest particles. The existing program for beam control was used to size particles of a known sieve size distribution between 45 and 105 μm and agreement between the SEM and sieve size analysis was good.

Figure 1 illustrates the principle of the SEM used in the microprobe mode on a coal particle. The electron beam excites a volume within the particle and the subsequent collection and analysis of the x-ray

Figure 1. Illustration of SEM Sampling of a Volume in a Coal Particle

fluorescence allows estimates to be made of the heavy elements present. However, the use of this technique on particles of known minerals (pyrite, feldspar, kaolinite, alumina, hematite) dispersed on C planchets gave deviations (90% of tests) from the mean of about 20 to 40%, which is entirely unacceptable for quantitative analysis. The same technique used on the minerals mounted in a resin matrix and polished gave standard deviations of about $\pm 5\%$. The problem is illustrated in Figures 2 and 3. The emitted radiation is subject to a widely variable adsorption path length for single irregular particles, thus giving the large standard deviations compared to the uniform path length in a polished specimen, see Figure 3.

On the other hand, the use of polished sections through particles suspended in a matrix has its own logical problem, as illustrated in Figure 4. A cross-section of a given size to the normal electron beam scan might have a large fragment of coal beneath it, or only a small fragment, so it is not possible to estimate the original size of the particle from the exposed cut. In addition, the excitation volume might lie outside of the coal fragment if the coal under the exposed section were a small fragment.

To test the effect of small particle size, the SEM-computer program was run on dispersed particles of known minerals of sizes below 10 μm , with a typical result as shown in Figure 5. It is seen that in addition to a wide deviation of results for a given size, the count response decreases with particle diameter. The deviation of counts for a given particle size was reduced by (a) counting only from a sampling point at the center of the particle cross-section (b) throwing out results from particles whose minimum to maximum diameters as measured by the movement across the particle were out of the range of 0.4 to 1. It was clear that the sampling excitation volume was exceeding the volume of the particles for the smaller particles or the narrow particles. Theoretical calculations on the expected excitation volume confirmed this. This volume can be reduced by lowering the beam voltage, but this then leads to long irradiation times to get suitable counting statistics.

In addition, experience with the existing program had shown a number of anomalies. The program logic was designed to move the beam until it recognized it was on a particle, find the center of the particle, measure four sampling points on the particle along directions at 45° angles around the center, and choose sampling points at the center and midway along the eight radii. By examining the bright spots on the particle image projected onto a cathode ray screen, corresponding to the chosen sample locations, it was found that there were many cases where the points were too close to the particle edge or even off the particle.

It was at this stage that it was realized that the existing CESEMI computer program would not be adequate for our purposes and that a developmental research program was needed. Analysis of the problems showed that under the existing logic a particle of mineral matter in the coal could make the beam believe it had reached the particle edge. An alternative logic was written to first trace the particle perimeter, thus defining the area for sample spot location. However, this program also gave anomalous results, and would sometimes lock on to a particle and

Figure 2. Illustration of operation of SEM on a dispersed sample.

Figure 3. Illustration of Operation
of SEM on a Polished Section

Figure 4 . Illustration of "cuts" through "cuts", for Mineral Matter in Coal Particles Suspended in a Resin

Figure 5. X-ray Counts Of Iron and Sulfur From Pyrite Particles

keep retracing it. This problem was traced to the difficulty of precisely defining the perimeter coordinates, because the position reached by the beam is defined by the time the beam moves, and, hence, depends on the beam velocity. Because of electronic rise-time and magnetic hysteresis problem, the velocity of the beam is variable as it is moved in short steps rather than continuously scanned over the whole surface. Thus, the edge of a particle appears to move as it is approached from different directions.

The steps taken to devise new techniques and new computer logic to reduce the problems are given in Sections 2.2 and 2.3 and the application of the resulting entirely new programs to coal particle analysis is given in Sections 2.5.1, 2.5.2, 2.5.3, 2.5.4.

1.5. Task 4 - Laboratory Tests on Slag Deposition

Figures 6 through 10 show the plane flame furnace which had been used previously at Penn State. The furnace is designed to operate on about 10 lbs/hr of pulverized coal premixed with air and give a plug flow of flue gas and burning particles down the furnace leg. The residence time in the hot region of the furnace is then comparable to that in a large boiler furnace, but the problem of residence time distribution caused by recirculation in a large furnace is avoided. Any particle goes through a very similar temperature-time history in the plane flame compared to any other particle.

However, preliminary test work on the furnace showed several problems for the desired purposes of the contract research. The samples collected at the base of the furnace leg showed excessive amounts of unburned carbon, and measurement of flame temperature gave rather low values. It was concluded from reading the previous reports of work on this furnace that it had always been run fuel-rich, which was very undesirable for tests designed to simulate boiler plant operation. The furnace was reconstructed with thicker walls (12.7 cm from 6.35 cm), but it was found that this produced only a slight increase in flame temperature. Preheating the air gave only a slight increase in flame temperature because the heat was extracted as the coal-air flowed through the stabilizer bank of water-cooled tubes.

Adequate flame temperatures were obtained by increasing the firing rate, but this caused the exit gas temperature to be higher than desired, since it was wished to place sample probes in a gas temperature corresponding to those at the top of a boiler. Consequently, the furnace was again reconstructed to increase the height of the leg.

This work had been performed using a commercially available pulverized coal (Pittsburgh Sea coal), since it involved many hours of furnace operation. It was found that different batches of this material were giving different peak flame temperatures and degrees of C burn-out. Size analysis showed the particle size distribution to be variable, and the supplier was unable to guarantee a fineness corresponding to normal pulverized coal. The extension of this work to eliminate the problems, the experimental techniques and the probe designs are discussed in Section 3.

Figure 6. Plane Flame Furnace Schematic

Figure 7. Diagram of Plane Flame Furnace Feeder System

Figure 8 Diagram of Vibrating Screwfeeder System

Figure 9. Section Showing Water-Cooled Flame Stabilizer

Figure 10 Detail of Cooling Water Tubes

1.6. Task 5 - Wetting and Contact Angle

The first tests were performed with a focussed, double reflector, arc-image furnace. A pellet of ash from the Keystone coal was melted on a polished graphite substrate, with the focussed beam of intense radiation producing a temperature between 1410 and 1490°C. The results were very erratic because vibration caused the beam to move on and off the pellet. Closing the shutter to cut off the beam caused the sphere of molten ash to freeze and it was removed for contact angle measurement on an optical bench. Only one out of every ten tests had contact angles within 7° of one another when measured at four points around the sphere-substrate interface. However, for tests where this criterion was met, there was clear indication that the contact angle decreased with time, from 150° to 117° after 5 minutes. The test was repeated for seven coals (analysis in Table 2) using a fixed melt time of 5 minutes, giving the result of Figure 11. It is clear that increased iron content reduces the contact angle, indicating more wetting of the carbon substrate. Addition of ferric oxide to an ash reduced the contact angle. Contact angles measured on a cast-iron substrate were less than 90°, showing spreading on the iron substrate.

Because of the poor reproducibility of the results from the arc-image furnace, an electric tube furnace was constructed with a viewing window. The sample pellet on a carbon substrate was pushed into the furnace, but it was found that it took 5 minutes to melt the pellet at a furnace temperature of 1450°C, because the sample and substrate acted as a heat sink. In an air atmosphere the contact angle increased with time up to 20 minutes and then decreased, as the carbon surface oxidized from the edge and reached the pellet-C interface. The same pattern of results was observed with several ashes and temperatures of 1300 to 1500°C. The maximum contact angle decreased at higher temperatures and was reached in shorter time.

The weight loss of the sample was complete within the approximate 20 minutes required to reach the maximum contact angle. The magnitude of the weight loss was proportional to the S content of the ash, and analyses indicated that the slags had lost all S at this time.

When tests were performed in an inert atmosphere, the contact angle on graphite increased to a maximum as before, but became constant and did not level off with time, see Figure 12. This, plus visual observation, indicated that the reaction between O_2 and the C substrate was the cause of the decrease in contact angle observed in air.

Measurements on a platinum substrate showed contact angles less than 90° after melting, which decreased to about 20° after 5 to 10 minutes. Tests on an alumina substrate showed contact angles decreasing from just above 90° to low values over 40 minutes of time, with clear evidence of reaction between the slags and alumina. The decrease in contact angle with time appeared to correlate with the calculated viscosity of the slags, that is, a slag of low viscosity spread more rapidly to give a low contact angle. The larger the mass of pellet the longer the time taken to spread on the surface.

TABLE 2

CHEMICAL COMPOSITION OF VARIOUS COAL LTA SAMPLES
(Weight % as oxide equivalents)

PSOC Sample No.	Source Area	ASTM Rank	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
002	Elkhorn No. 3 SEAM; Mine 22, Kentucky	HVA	59.5	26.7	4.2	3.4	2.3	0.7	0.8	0.1	1.8
006	Elkhorn No. 3 SEAM; Mine 22, Kentucky	HVA	56.1	29.1	2.9	3.2	2.9	0.6	0.9	0.1	3.4
012	SEAM C Mine 1, Kentucky	HVA	52.3	29.2	6.7	1.7	2.2	0.9	1.9	1.7	2.7
013	SEAM C Mine 1, Kentucky	HVA	43.5	30.8	9.7	1.7	3.2	0.6	3.9	0.3	4.2
021	Illinois No. 6 SEAM Mecco Mine, Illinois	SUBBIT A	50.0	22.2	10.8	0.9	9.0	1.1	0.4	2.2	1.6
025	Illinois No. 6 SEAM Sahara Mine No. 6, Illinois	HVC	46.5	20.3	26.5	0.9	1.0	0.8	0.3	2.2	0.8
081	Buck Mountain Renninger Mine, Pennsylvania	AN	50.1	34.3	5.2	3.3	2.1	1.3	0.2	0.8	2.6

Figure 11. Variation of Contact Angle with Chemical Composition
Temperature, 1410 degrees C; Time of Exposure, 5 minutes;
Substrate, Graphite.

Figure 12. Variation of Contact Angle with Time for Different Coal-Ash Samples. Substrate: Graphite, Atmosphere: Argon, Furnace Temperature: 1420 degrees C.

At this stage, it was concluded that the non-equilibrium nature of the above experiments made it difficult to draw quantitative conclusions. In addition, the test procedure could not be extended to steel substrates because they melted in the furnace. Attempts to control the substrate temperature by air, water or oil flow through the substrate in the furnace were unsuccessful. An entirely new approach was necessary. A redefinition of the objectives of the wetting tests was: it is desired to measure the wetting-adhesion interaction of a well-melted drop of slag (melted in a short time under conditions comparable to those in a flame) with a metal substrate held at a temperature corresponding to the metal surface in a boiler tube. The drop will solidify on contact with the substrate, and the apparent contact angle measured cannot be an equilibrium value, but it will indicate more directly a property relevant to the boiler slagging problem.

The development of this line of thought is discussed in section 2.4 and the results of the new test are given in sections 2.5.5, 2.5.6 and 2.5.7.

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SECTION 2. A STUDY OF COAL ASH WITH RESPECT TO SLAG DEPOSITS

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2.1 Introduction

Of the roughly 3.5 billion metric tons of coal mined all over the world, about 60 percent is pulverized for combustion in boiler furnaces. Since such coals are not generally subjected to any cleaning process, large amounts of non-combustible inorganic material in coal find their way into the boiler furnaces. To get a feel for this amount, a typical coal-fired power station of 1000 MW capacity using coal with 10% ash, would be fed with roughly 250 tons of this inorganic material in a day. Seventy to 90% of this escapes from the furnace as fly ash. The rest of the inorganic material forms a molten phase in the furnace and may run along the heat exchange surfaces to the bottom of the furnace as liquid slag or falls into the bottom of the furnace as agglomerates of ash. Some portion of this slag always remains in the furnace, leading to deposits on the heat exchange surfaces.

From the standpoint of boiler operation, it is always desirable to operate the boiler under conditions that lead to minimum slag formation since this slag creates a number of problems in the boiler. Due to the insulating nature of this slag, accumulation on heat transfer surfaces causes greatly increased resistance to heat transfer. There have been steam generators built in which the design rate of heat release in the furnace could not be maintained because of ash deposits from the coal,

requiring extensive subsequent modifications of the plant. These deposits in the upper regions of the furnace also alter the flow patterns of combustion gases, causing derated operation and complete outages. In addition these deposits can accumulate in the upper regions of the furnace until their mass can no longer be supported. Thus, the lower parts of the boiler furnace are susceptible to damage by the falling mass of slag.

The most commonly used approach to reduce slag accumulation is to operate a boiler at a lower exit gas temperature and consequently a lower steam temperature. The thermodynamics of the Rankine steam cycle, however, show that the highest efficiencies are obtained when the temperature of the steam entering the turbine is as high as possible. The alternate solutions to this problem have met with little success. A clear understanding of the principles behind slag deposition and accumulation might enable alternative solutions to be found. The present study was undertaken with the objective of understanding the fundamental principles of sticking, wetting and adhesion behavior of coal fly ash to the heat exchange surface.

2.1.1. Statement of the Problem

To understand the approach adopted in this study, it is necessary to look at the physical transformation of the mineral grains within a coal particle during its combustion under pulverized coal flame conditions.

The pulverized coal particle (size 100 μm and below) upon entering a combustor, is heated to peak furnace temperatures of

1400°C to 1700°C (depending on coal type and operating conditions) at very high heating rates exceeding 10^5 °C/sec. During this process, coal particles undergo a rapid devolatilization, coking with some swelling and burning. The studies on single particles subjected to these conditions in the laboratory have indicated that: (a) the coal particles do not explode during devolatilization and (b) each particle generally results in the formation of thin-walled hollow spheres also referred to as cenospheres. These cenospheres finally disintegrate leading to ash particles. During the formation of cenospheres it has been observed by Sarofim et al (1) that negligible amounts of mineral matter are expelled from the particle. In the same study it was found that even though bituminous coal particles swelled by factors of four or five in linear dimensions during the devolatilization process, the mineral matter was retained by the carbonaceous matter forming the shell of a cenosphere. Even the molten mineral particles remained attached to the receding carbonaceous surface.

It is expected, therefore, that during combustion, the mineral grains within the coal particles would be drawn together and agglomerate leading to bigger ash particles. In fact this agglomeration has been observed by several investigators notably Ramsden (2), Lightman et al (3), Mitchell et al (4), Paulson et al (5) and Street et al (6). There is some question as to whether this agglomeration leads to one particle or more than one particle within a cenosphere. Sarofim et al (1) estimated through indirect means that between one and five agglomerates are formed in each particle and the number of such agglomerates formed is indepen-

dent of the original size of the coal particle and temperature of the flame. Upon disintegration of the cenosphere each agglomerate in the coal particles would result in one ash particle. It is obvious then that compositions of these ash particles would depend on the average mineral composition of the coal particle that it originated from. Since the composition of the individual particles of coal vary to a considerable degree from each other, the composition of these ash particles would also vary. As a result it would be erroneous to predict the composition of these ash particles from the bulk ash analysis of the coal sample as a whole. The only way to predict the composition of the ash particles would be to perform a chemical analysis of the coal sample on a particle-by-particle basis.

During their flight in the combustor it is possible that some of the ash particles could further collide with one another leading to further agglomeration. The probability of such collisions is small, and it is expected that most of the ash particles would not under go any further agglomeration.

Due to the intense turbulent conditions inside the boiler there would be a finite probability of collisions of these ash particles with the heat transfer surfaces. This probability is not expected to be the same for all particles, i.e., all ash particles do not stand an equal chance of striking the heat transfer surfaces. Upon collision with the relatively cold heat transfer surfaces, the ash particles, depending on their composition, would either stick to the surface or simply bounce off. It is the sticking particles

that would contribute to the ash and slag deposition on the furnace walls. This sticking is characterized by the ash particle-metal interaction. It is possible that the metal might have already been coated with deposits (from previous sticking collisions) or an alkali salt vaporized from the coal particles during combustion and condensed on the colder heat transfer surface. In such a case the sticking would be characterized by ash particle-slag/salt-metal interaction. In either case, the temperature of the particle is expected to be from 1000°C to 1700°C and the temperature of the metal would be 200°C to 700°C. Both these interactions would be strongly dependent on the composition of the ash particle.

Therefore, to understand the slagging behavior of a coal sample, the following information would be necessary:

- i) inorganic element composition of each representative coal particle in the coal sample
- ii) interaction of ash particles of various compositions heated to high temperature with a relatively colder metal surface
- iii) interaction between ash particles and metal surfaces coated with different inorganic salts

From a knowledge of the composition of the inorganic elements of individual coal particles, it is possible to estimate the composition of ash particles by assuming that each coal particle would lead to ash particles of similar composition to the parent coal particle.

It is not physically possible to study ash-metal and ash-ash-metal interactions for all the possible compositions of ash particles that would have resulted from a coal sample. Instead it is feasible to perform a selected number of tests with synthetic mixtures of typical coal minerals and establish some general trends to allow the prediction of the interaction for actual ash particles. The experimental conditions for these studies should include a method of rapidly heating a mineral composition to a high temperature followed by bringing it in contact with a colder substrate of either a metal or a coated metal. Upon contact, the equipment should be able to estimate the extent of sticking of the synthetic mineral mixture to the substrate. Section 2.4. discusses the apparatus designed for this purpose.

2.1.2. Bibliography

There is an extensive amount of literature available on the subjects of coal ash slags, deposit formation, fouling, slagging and related phenomenon. The major emphasis of much of the previous work is in thermal transformation of mineral matter in coal, chemistry of compounds that are formed from mineral matter upon combustion of coal, mechanisms of deposit formation and correlation of the chemical compositions of the mineral matter with flame temperature, fusibility, viscosity or some other property of the slag, in order to predict slag phenomena in the furnace.

The compositions and the thermal transformations of the mineral matter in coal has been extensively viewed by numerous investigators; including Theissen (7), O'Gorman (8), Reid (9), Borio (10), Whittingham (11), Watt (12), Nelson (13) and Padia (14). The bulk of the mineral matter in coals comes from five main groups: oxides, clays, kaolin, sulfides and carbonates. Oxides are present as quartz and hematite. The clays include illite, muscovite and montmorillonite. A typical kaolin mineral is kaolinite. The sulfides consist mainly of pyrite and marcasite, whereas carbonates present are predominantly calcite and dolomite. Besides shales, feldspars and biotites, alkali compounds may also be present as chlorides. Most of these papers also contained discussions of the thermal transformations of various minerals upon heating. However, the experimental studies quoted were usually carried out at low rates of heating (10-100°C/sec), whereas in actual pulverized coal firing the heating rates to which the minerals are subjected vary from 10^5 - 10^6 °C/sec. It is not clear in every case whether the heating rates would influence the transformations, but it is certain that it does in some cases. A detailed and excellent review of the thermal decomposition of various minerals in coal is provided by Watt (15) in a BCURA report.

A considerable amount of work has been done to predict the slagging behavior of a pulverized coal from the mean ash compositions of the whole coal. It has been attempted by various workers to correlate the slagging behavior of a coal with properties such as slag viscosity (9,16,17), temperature of critical viscosity (18,19) and fusion temperature (20). Empirical factors such as the slagging factor (21,23), fouling factor (21,23), dolomite percentage (22), ferric percentage (23),

and base-to-acid ratio (9), all calculated from bulk ash composition, have been devised to predict the behavior of ash in coal fired boilers. Although these indices are often of use in detecting an obviously bad coal, in many cases they are not precise enough to ward off slag problems. Many of the indices are only useful within a small range of composition and for certain furnace types. It is concluded that a much more in-depth understanding of the slagging phenomenon and mechanisms is essential before it is possible to accurately predict the slagging behaviour of a coal from its compositional data.

The mechanisms of deposit formation have also been studied in detail. Hodson (24) in studies related to corrosion in preheaters, suggested that oxides of sulfur and water vapor formed sulfuric acid which reacted with the iron from the heat transfer surfaces. Crossley (25), Reid (9), Crone (26) and Corey et al (27,28) attributed the build-up in the boiler to alkalies present in the coal. These alkalies are thought to vaporize during combustion and then condense on heat transfer surfaces. They then react with the SO_3 in the combustion gases, and the metal oxide on the heat transfer surfaces to form low melting alkali metal sulfates which act as a glue to add fly ash particles. This mechanism appears to be fairly well proven for fouling in the convective superheater passes, although much remains to be learned why some alkali-bonded deposits are strongly sintered to the tubes, while others are loose and friable. Crossley (25) also mentions the possibility of acids of phosphorous forming and condensing on the boiler tubes, but only in retort stokers due to the long times at highly reducing conditions and high temperature in the fuel bed. With respect to wall slagging, Gumz (29) suggested that very fine particles formed the first

layer of deposit, on which larger particles then built up as the insulating nature of the layer caused it to become hotter and sticky.

However, none of these papers offer fully convincing explanations as to why the first layer of wall slag sticks to the tubes. Though many felt the need of understanding the sticking mechanism of deposits to metals, Watt (12,15) and Reid (9) were the first to realize the similarity between the industrial operation of enamelling and slag deposit formation. Most of the oxides used in enamels, e.g. SiO_2 , Al_2O_3 , Na_2O , K_2O , Fe_2O_3 , MgO and CaO are also present in coal ash slags. The base metals used in enamelling are the same as the metals used for heat transfer surfaces in boilers, namely, iron and steel alloys. An extensive literature is available regarding the mechanisms of sticking, wetting and adherence of ceramic oxides to metals in the enamel and ceramic literature (see below).

For a liquid oxide to adhere to a metal, it must be able to wet the surface. The extent of this wetting is estimated by the contact angle that the liquid makes with the solid surface. By convention, contact angle is always measured on the liquid side and the lower the contact angle the better the wetting. The contact angle has been found to be a function of temperature and oxygen partial pressure (30). The contact angle increases (degree of wetting decreases) as the atmosphere changes from oxidizing to neutral to reducing (31,33). Incorporation of iron oxide in a glass was found (32) to reduce contact angle or enhance wetting on an iron substrate. Ohmine (34) found that contact angle of coal ash slags on platinum and graphite decreased with increased temperature and followed similar trends to the viscosity of these slags.

The two main theories of an adherence mechanism in enamelling discussed by various authors [Laszlo (35), Dietzel (36), Lord (37), Kautz (38), Richmond et al (39) and King et al (31)] may be classified either as chemical or mechanical. The chemical theory attributes the adherence in enamels to the chemical bonding between the oxide and the metal through the formation of a common interface. The driving force for the formation of interface is the achievement of thermodynamic and chemical equilibrium between the species at the point of contact of metal and oxide. Three main mechanisms proposed for achieving this equilibrium are (i) the FeO interface theory (ii) the dendrite theory and (iii) the electro-chemical theory. Proponents of the mechanical theory (35,39) attribute the adherence to the mechanical gripping between oxide and metal.

More recently Pask et al (40) felt that both the chemical bonding and mechanical gripping are important in the adherence between slag and metal. Both factors are thought to contribute to the strength of the interface. These authors concluded that for good adherence the interface should be saturated with an oxide of the base metal, which in case of iron or steel would be FeO. King et al had earlier suggested that for good adherence, the oxide of base metal when in solution in the enamel should be such as not be reduced by the metal.

The so-called adherence oxides that promote adherence in enamels have been studied by many workers (31,40,41). Healy et al (41) identified oxides of tungsten, osmium, rhenium, technitium, molybdenum and cobalt as the adherence promoters, because these oxides are reduced by iron and their metallic forms have unit cell dimensions similar to iron. King et al (31) on the basis of free energies of formation predicted that Ca, Bi, Ni, Mo, Co, As and Pb oxides would be adherence promoters because

of their being reduced by and precipitated onto iron base metal.

Pask et al (40) defined good adherence promoters as the oxides that besides being reduced by iron would in their reduced state be able to form continuous solid solutions with the iron.

Karamis (42) and Dietzel et al (43) reported that sulfides also act as adherence promoters. The sulfur-bearing enamels showed better wetting ability. They also developed strength under moderate firing conditions. Still (44) and Kato et al (45) found that adherence of oxides to steel is also a function of the carbon content of the steel. The adherence was found to improve as the carbon content of steel increased.

Further pertinent literature is cited in the following sections at those places where it is most relevant to the research techniques and results.

2.2. Analysis of Coal Particles: General Principles

2.2.1. Introduction

A technique developed at this University, the Computer Evaluation of Scanning Electron Microscope Images (46) (CESEMI) was used for this purpose. The 'CESEMI' method essentially involves scanning a focused electron beam over a particle surface, collecting secondary electrons or back scattered electrons and thereby generating a two dimensional image of the particle, which is analyzed to determine the size and area of the cross section of the particle. Since a large number of particles (usually in the thousands) is involved, the analysis is performed with the help of a minicomputer. After the computer has evaluated the size, shape and area of a particle, the electron beam is brought to rest on the particle at one or more points for a suitable length of time to generate characteristic x-rays from the particles. It is then possible to estimate the chemical composition of the particle from the wavelength and the intensity of the x-rays. The particles to be analyzed may be prepared by either of the following methods (i) dispersed on a suitable substrate or (ii) embedded in a pellet of an organic resin followed by polishing a section through the pellet to expose cross sections of the coal particles.

2.2.2. General Principles

The basis of this technique is the electron-particle interaction. It is the unique nature of this interaction that makes a computerized scheme of particle analysis possible. This interaction produces (besides other radiations), secondary electrons, back-scattered electrons, characteristic and continuum x-rays.

The secondary electrons are produced by the inelastic collisions occurring between the loosely bound outer electrons of the atom and the incoming electron beam. The intensity of the secondary electron signal depends primarily on the particle topography and has little dependence on the atomic number of particles. As a result the secondary electron signal gives a good contrast for coal particles that are dispersed on a suitable substrate. On the other hand the signal gives a poor contrast between coal particles and a surrounding matrix for polished sections of coal particles embedded in an organic resin.

The back-scattered electrons result from the elastic scattering of the electron beam by the Coulombic field of the nucleus of the atom. The extent of scattering depends primarily on the atomic number of the atoms in the target material. Thus particles with different atomic numbers would result in different intensities of the electron back-scatter signal. In addition to atomic number, intensity of the back-scattered electrons is also a function of the topography of the particles. Therefore a contrast (between particles and background) based on a combination of topographical and chemical difference will result for particles dispersed on a

substrate. On the other hand, when the particles are embedded in a resin and then polished, the contrast results because of the difference in atomic number between the resin and the particle.

The x-rays are generated as a result of core scattering and inner shell ionization by the collisions of the electron beam with the atom. The core scattering results in the emission of continuum radiation. The inner shell ionization leads to the production of characteristic x-rays. The wave length of the characteristic x-rays is unique for each element and hence can be used for chemical identification. The intensity of characteristic x-rays depends on the concentration of the particular element present in the particle. There is a specific emission volume from which the x-rays are generated within the particle. The size and shape of the emission volume depends on the atomic number of the particle. For all coal particles it is expected to be pear-shaped. The diameter of the emission volume depends on the density and composition of the particle and can be roughly estimated from Kanaya and Okayama's equation (47) as

$$\rho D = 0.0276 E_0^{1.67} A/Z^{0.9} \quad (2-1)$$

where E_0 is the acceleration voltage in kV, A the average atomic weight of the particle, Z the average atomic number of the particle, ρ the density of the particle in gms/cm^3 and D the diameter of the emission volume in micrometers.

2.2.3. Hardware Requirements

To perform size and chemical analysis of the coal particles using a scanning electron microscope, the hardware system must be capable of the following actions, at least:

- i) be able to distinguish a particle from the background
- ii) have some built-in mechanism to record distances while the electron beam moves on a particle along a line scan,
- iii) collect the x-rays for a specified time from the particle
- iv) separate the characteristic x-rays according to their energies
- v) record the intensities of the x-rays of certain wavelengths
- vi) be able to perform some computations and put out the results.

The first objective, distinguishing a coal particle from the background, may be achieved by monitoring the secondary electron signal or electron back-scatter signal from the specimen. In the case of a dispersed sample either signal would provide enough contrast to distinguish a coal particle from the substrate it is resting on. In the case of a polished section of the coal particle embedded in a resin, only the electron back-scatter signal may provide the necessary contrast under certain conditions. For a particle to be identified from the surrounding resin by the electron back-scatter signal, it is necessary that there be a differ-

ence in atomic number between the coal particle and the resin. This may be achieved by making the resin from a material of higher atomic number than coal (a resin with a lower atomic number than coal would be difficult to make). Figure 1 (a and b) illustrate the intensity of various signals from dispersed and polished sections of coal particles.

The second objective requires considerable hardware modifications. The hardware system should be designed to control the position of the beam on a slide and be able to move it to any desired position, receive feed-back from the secondary electron or electron back-scatter detectors to recognize when the beam is on a particle and estimate the distance that the beam travels while moving from one point to another on the slide. Objectives (iii), (iv) and (v) can be met by attaching an energy dispersive system and an x-ray multichannel analyzer to the SEM. The multichannel analyzer system should also have some memory to store the digitized x-ray intensity and a digital clock to record the time of collection of x-rays. The last objective may be achieved by interfacing an SEM with a minicomputer.

The CESEMI system available at the Materials Research Laboratory of The Pennsylvania State University achieves these objectives by incorporating special electronic hardware into the scanning electron microscope and interfacing it with the computer. A brief discussion of this system is presented in the next section. For complete details of the CESEMI system, the reader is referred to a thesis by J. Lebieczik. In the discussion that follows, it is

Figure 1. Intensity of SE and EBS signal from: a) a coal particle dispersed on carbon or beryllium substrate b) a polished section of the coal particle embedded in a suitable resin.

assumed that the reader is familiar with the working of a scanning electron microscope.

2.2.4. CESEMI System

A schematic block diagram of the CESEMI system is shown in Figure 2. The image-forming part consists of a JOEL model 50A SEM fitted with x-ray, secondary electron and back-scattered electron detectors. There are four back-scatter electron detectors connected together to one common electrode so the signals from these detectors are summed and fed into a single amplifier. Both the secondary electron and the back-scatter electron signals are analog signals, while the characteristic x-ray signals are digital. So, for the secondary electron and the electron back-scatter signals, an analog comparator is used to make the decision as to when the beam is 'ON' or 'OFF' the particle by comparing the intensity of the signal from the particle to that of a preset level of background. The signal from the comparator is digitized by an analog-to-digital-converter to report '1' for ON and '0' for OFF the particle to the interface. The interface consists of a standard general purpose interface DR-11A, supplied by Digital Equipment Corporation, Maynard, Massachusetts. The PDP-11/20 computer, which accesses the scanning electron microscope through this interface is also supplied by Digital Equipment Corporation. It has a 32K memory with 16 bit words. Of the 32K only 28K are available to the user, the rest being reserved for the operating system. The computer is also provided with two large secondary storage devices for bulk storage of the data and programs.

Figure 2. Schematic diagram of the 'CESEMT' system.

The electron beam is controlled by the computer through a randomly addressable digital-controlled scan generator. The latter consists basically of two 12 bit registers for storing horizontal (x) and vertical (y) coordinates and two fast digital-to-analog-convertors with buffer amplifiers and interaction circuitry. Any point density up to 4096×4096 can be selected for digital scanning in a point-by-point manner with a precision of one part in 4096.

The x-ray collection system consists of a solid state x-ray measurement device and a multichannel analyzer. As mentioned earlier, the x-ray signal is a digital signal and can be stored directly as such in eight 16 bit counters. Each counter actually consists of two eight bit registers, with the maximum capacity of each counter being 65535 ($2^{16}-1$). The contents of the counter are fed to the computer via a digital multiplexer directly without decoding. The selection of a particular counter and time of collection is decided by software.

The scanning electron microscope accepts a 16 bit word from a register (specified by address 167772) in the interface. This word is composed of 12 bits of data and four bits of destination. The destination may be either the digitally-controlled scan generator or the x-ray channel, so that the data may enter or leave from either of these by specifying a particular bit configuration. A bit configuration of 0001 or 0010 would instruct the scan generator to move the beam to a horizontal position or a vertical position respectively. A bit configuration of 0011 or 0100 would

be an instruction to the x-ray channels, the former to set up the x-ray channels to collect the x-rays and latter to retrieve the data from the channel. The interface accepts data from the SEM (either from x-ray channels or the detectors) in a 16 bit register specified by address 167774.

2.2.5. Software Requirements

To be able to analyze the size and elemental composition of the particles using the above CESEMI hardware, the software should: construct a two-dimensional image of the particles to estimate the cross sectional area of the particle and the x-ray sampling points on the particle from where the x-rays will be collected; position the beam over the sampling points to collect x-ray, and convert the x-ray counts into weight percentages of elements. To build a two-dimensional image of the particles, it is necessary to ensure that the comparator reports ONE to the interface when the beam is on a particle and ZERO when the beam is on the background. This is easily achieved for dispersed coal particles by using the secondary electron signal as shown in Figure 3. For polished samples of coal particles embedded in a resin of higher atomic number than coal, this poses some problems. In such a case, the electron back-scatter signal from the background is in some cases even brighter than the mineral matter. For using computer control, this signal must be inverted so as to make the coal particles look bright and the resin dark. However, this may also make the mineral matter (higher atomic number than coal) look

Figure 3. Signal monitoring from a) dispersed coal particles b) polished sections of coal particles.

darker as shown in Figure 3. This means that to define a particle, the software cannot rely on the reported status of those points that are inside the particle, since some of them may be reported as background whereas actually these are mineral grains in the particle. One possible solution to this problem is to define a particle by its perimeter points only. This was the method used in this study. We have observed that mineral grains associated with the coal particles (of sizes 100 μm and below) generally lie within the particle and not at the edges, so that if a particle is traced along its edges, then the perimeter points so generated would describe the particle without any ambiguity.

The second objective of collecting x-rays is achieved by supplying x-y coordinates of the x-ray sampling point to the interface and positioning the beam on these points to generate the x-rays. The electron beam on each of the sampling points activates a certain volume whose diameter can roughly be calculated by equation 2-1. For coal particles this diameter is 6-8 μm at acceleration voltages of 18-25 kV. That would mean the sampling points should be chosen by fitting as many complete circles of 6-8 μm diameter as possible to cover the maximum cross-sectional area of the particle. In the present study 8 μm was chosen as the diameter of the test spot. The x-rays generated from these test spots are collected by setting up the x-ray channels for the correct energy and digital clock for a suitable length of time. The time of collection of x-rays has a strong bearing on the accuracy of the measurement. This is because the x-ray genera-

tion is a random phenomenon, which implies that a large number of repetitive measurements of x-ray counts for a fixed and finite time under unchanged conditions would yield a statistical distribution of the number of x-rays counted. Clearly, this effects the reproducibility of a set of x-ray measurements on the same sample. It can be mathematically derived that this error is a function of the number of x-rays counted. Without going into details, the counting error is expressed as

$$\text{counting error} = \sqrt{N} \quad (2-2)$$

and

$$\text{relative error} = \sqrt{N}/N = 1/\sqrt{N} \quad (2-3)$$

where N is the number of x-ray counts. This analysis is based on the assumption that the statistical distribution of the x-ray counts follows a Gaussian function. For 400 counts, the error is 0.05 or 5%.

The last objective of converting the x-rays into weight percentages needs some elaboration. The most common method of obtaining weight percentages from x-ray counts is by a method called the ZAF Correction Procedure, where Z denotes the atomic number correction factor, A the absorption correction factor and F the fluorescence correction factor.

2.2.6. The ZAF Correction Procedure

The basis of this method is that the ratio of the intensity of the characteristic x-rays generated from an element A in a particle to those generated from pure A in a standard, referred to

as the 'k' ratio, is directly proportional to the concentration of element A in the particle. This assumption is valid if element A is uniformly present at the atomic or molecular level and particle thickness is greater than the x-ray range. However, in coal, the mineral matter is not distributed uniformly at the atomic or molecular level, so the method is not ideally suited for the coal particles. In the discussion presented, the values of various parameters are given for five elements only, Al, Si, S, Ca and Fe (these being the ones that were analyzed in the coal particles during this study).

In this method the k ratio is corrected for the following effects:

- 1) the difference in electron scattering and retardation in the specimen and standard, i.e., the so-called atomic number effect ($k(z)$)
- 2) absorption of x-rays within the particle ($k(A)$)
- 3) the fluorescence effect i.e. the characteristic x-rays of one element generating characteristic x-rays of another element in the particle ($k(F)$)
- 4) fluorescence due to continuum x-rays ($k(e)$)

A common form of the correction equation is then

$$C = k \cdot k(z) \cdot k(A) \cdot k(F) \cdot k(e) \quad (2-4)$$

where C is the weight fraction of the element of interest. Most of these correction factors have been empirically deduced and different workers have expressed these factors in different forms.

The various forms generally lead to similar values and the equations presented in this discussion are the ones used in the present study.

The correction factor $k(z)$ arises because of the atomic number difference between the specimen and the standard. This leads to differences in the yield of back-scattered electrons and the x-ray emission volume. A higher yield of back-scattered electrons for the higher atomic number element means that fewer electrons are available for x-ray excitation and vice versa. A higher x-ray emission volume would lead to higher x-ray yields and vice versa. It has been shown (49) that $k(z)$ can be approximately estimated by the following equation

$$k(a) = \frac{B(s) \times S}{B \times S(s)} \quad (2-5)$$

with small errors (50). In the above equation $B(s)$ and B are back-scattering correction factors for the standard and specimen respectively. The stopping power essentially determines the x-ray emission volume. A higher stopping power element would stop the beam at a shorter penetration depth and hence result in lower emission volume.

The value of the back-scatter factor (B) for an element i in a mixture of elements $1, 2, 3, \dots, i, \dots, n$, is given (51) by the equation,

$$B(i) = \sum_{j=1}^{j=n} C(j) \times BB(i, j) \quad (2-6)$$

The value of $BB(i, j)$ may be computed (52) from the following equation

$$BB(i,j) = R1(i) + R2(i) \times \ln(R3(i) \times Z(j) + 25) \quad (2-7)$$

where

$$R1(i) = 8.73 \times 10^{-3} U^3(i) - 0.1669 U^2(i) + 0.9662 U(i) + 0.4523$$

$$R2(i) = 2.703 \times 10^{-3} U^3(i) - 5.182 \times 10^{-2} U^2(i) + 0.302 U(i) + 0.1836$$

$$R3(i) = 0.887 U^3(i) - 3.44 U^2(i) + 9.33 U(i) / U^3(i)$$

$$U(i) = E_o / E_c(i), \text{ if } E_o / E_c(i) > 10 \text{ then } U(i) = 10$$

E_o = acceleration voltage in kV

$E_c(i)$ = critical excitation voltage for the element i in kV

$C(j)$ = fractional concentration of element j in the mixture and

$Z(j)$ = atomic number of element j .

Table 1 lists the value of E_c , and Z for seven elements C, O, Al, Si, S, Ca and Fe. Table 3 lists $BB(i,j)$ values for elements Al, Si, S, Ca and Fe calculated by using the above equations at $E_o = 20$ kV.

The values of stopping power (S) for an element i in a mixture of elements $1, 2, 3, \dots, i, \dots, n$, is given by

$$S(i) = \sum_{j=1}^{j=n} C(j) x_{ss}(i,j) \quad (2-12)$$

The value of $ss(i,j)$ can be calculated by the equation of Bethe (53) as

$$ss(i,j) = (Z(j)/A(j)) \times (1/EE(i)) \times \ln(1166 \times EE(i)/J(i)) \quad (2-13)$$

where $J(j)$ (in eV) is the mean ionization potential of element j . $J(j)$ may be calculated from the equation given by Berger

and Seltzer (54) as

$$J(j) = 9.76 Z(j) - (58.8/Z(j))^{0.19} \quad (2-14)$$

It has been proposed by Thomas (55) that the value of $EE(i)$ may be taken to be $0.5(E_o + E_c(i))$ with little loss of accuracy. Table 4 lists the $ss(i,j)$ values for five elements Al, Si, S, Ca and Fe at $E_o = 20$ kV. The values of Z , A , J and E_c used in this equation are listed in Table 1. $J(i)$ values listed in Table 1 were calculated from equation 2-14.

The absorption correction factor ($k(A)$) arises because emerging characteristic x-rays are absorbed to different extents by the specimen and the standard. The value of $k(A)$ is given by

$$k(A) = A(s)/A \quad (2-15)$$

where $A(s)$ and A are the absorption correction factors for the standard and the specimen respectively. The value of the absorption correction factor for element i in a mixture of elements $1, 2, 3 \dots i \dots n$ may be obtained by the equation proposed by Heinrich (56) as

$$1/A(i) = 1 + 3 \times 10^{-6} (E_o^{1.65} - E_c^{1.65}) X(i) + 4.5 \times 10^{-13} (E_o^{1.65} - E_c^{1.65}) X^2(i)$$

which may be approximated by

$$1/A(i) = [1 + 1.2 \times 10^{-6} (E_o^{1.65} - E_c^{1.65}) X(i)]^2 \quad (2-16)$$

Table 1
Physical Constants

Element	A	Z	$E_c(\text{keV})^{(62)}$	$J(\text{eV})$	$W^{(63)}_{E_0} \frac{1.65}{-E_c}$	$\frac{1.65}{-E_c}$
C	12	6	0.284	100	0.0009	-
O	16	8	0.532	117	0.0022	-
Al	27	13	1.56	162	0.038	138.1
Si	28	14	1.84	172	0.038	137.45
S	32	16	2.47	190	0.098	135.74
Ca	40	20	4.038	228	0.166	130.20
Fe	56	26	7.111	285	0.310	114.70

Table 2
Mass attenuation coefficients for $K\alpha$ lines⁽⁶⁴⁾

Absorber	emitter				
	Al	Si	S	Ca	Fe
C	557	357	160	42	9
O	1503	966	436	116	25
Al	386	3493	1594	432	93
Si	506	328	1950	530	116
S	794	518	240	765	167
Ca	1667	1086	502	140	296
Fe	3841	2502	1157	321	71

Table 3

BB(1,j) Values

j	i				
	Al	Si	S	Ca	Fe
C	0.95	0.95	0.958	0.969	0.987
Al	0.9	0.9	0.917	0.924	0.946
Si	0.893	0.893	0.912	0.918	0.94
S	0.880	0.880	0.901	0.906	0.93
Ca	0.855	0.855	0.881	0.884	0.91
Fe	0.821	0.821	0.958	0.853	0.882

Table 4

ss(1,j) values

j	i				
	Al	Si	S	Ca	Fe
C	0.224	0.222	0.217	0.205	0.186
O	0.217	0.215	0.210	0.199	0.181
Al	0.194	0.192	0.188	0.178	0.162
Si	0.199	0.197	0.193	0.183	0.167
S	0.194	0.193	0.188	0.179	0.163
Ca	0.186	0.184	0.180	0.171	0.156
Fe	0.163	0.161	0.158	0.150	0.137

where $X(i)$ is the absorption parameter given by

$$X(i) = \sum_{j=1}^{j=n} C(J) \times M(i,j) / \sin\theta \quad (2-17)$$

$M(i,j)$ is the mass attenuation coefficient of the element i in element j and θ is the angle between the particle surface and x-ray detector, the take-off angle. Table 2 lists the mass attenuation coefficient of five elements Al, Si, S, Ca and Fe. Table 1 lists the value of $E_o^{1.65} - E_c^{1.65}$ for $E_o = 20$ kV for these elements.

One important aspect of the absorption correction factor needs to be emphasized. The equations derived for this factor equations 2-16 and 2-17, assume that x-rays are leaving a flat surface. This assumption is essential for the estimation of absorption path lengths which enter into the derivation of these equations. The assumption is satisfied only by the polished samples and not by the dispersed samples. This becomes evident from Figure 4, where the x-ray absorption path is shown for a dispersed coal particle and for a polished section of the coal particle. It is seen from Figure 4 that for the dispersed sample, the absorption path length (shown by dotted lines) is different for different sampling points on the same particle. The absorption correction factor can be estimated for this particle only after knowing the topography of the particle. On the other hand for the polished specimen shown in Figure 4, the x-ray path length is constant at $R/\sin\theta$ and one general equation would describe the correction factor for all the x-ray sampling points.

Figure 4. Absorption path length from a) dispersed coal particles b) polished sections of coal particles.

For the third correction factor, the characteristic fluorescence x-rays are generated if the energy of the characteristic peak $E(i)$ for element i in a specimen containing element j is such that $0 < (E(i) - E_c(j)) < 5$ kev where $E_c(j)$ is the critical excitation necessary to eject electrons from the inner, K, L or M shell of element j . Then, parasitic fluorescence will be produced for the element j . As a result more x-rays of element j are present than would have been produced by electron excitation alone. Since the composition of the standard and the coal particle are different, this effect will be different for the two and must be accounted for. The value of this correction factor depends very much on the x-ray line used. In the present study, $K\alpha$ lines were used and the following discussion is valid for $K\alpha$ lines only. However, changing to a different line does not alter the reasoning or the form of the equations.

For an element i in a mixture of elements $1, 2, 3, \dots, i, \dots, n$, the form of the equation is

$$f(F) = \frac{Fl}{Fl(s)} \quad (2-18)$$

where $Fl(s)$ and Fl are the fluorescence correction factors for the standard and the specimen, respectively. The value of Fl may be calculated by the equation given by Reed (57) as

$$Fl(i) = \frac{1}{1 + \sum_{j=1}^{j=n} r(1,j)} \quad (2-18a)$$

where

$$r(i,j) = 0 \text{ if } 0 \geq E_c(j) - E_c(i) > 5.0$$

otherwise if

$$0 < E_c(j) - E_c(i) \leq 5.0 \quad (2-19)$$

then

$$r(i,j) = C(j) \times Y_0 \times Y_1 \times Y_2 \times Y_3 \quad (2-20)$$

where

$$Y_0 = 0.44 \times w(j) \times A(i)/A(j) \quad (2-21)$$

$$Y_1 = [(U(j) - 1)/(U(i) - 1)]^{1.67} \quad (2-22)$$

$$Y_2 = M(j,i)/M(j,x) \quad (2-23)$$

$$Y_3 = \frac{\ln(1+U)}{U} + \frac{\ln(1+V)}{V} \quad (2-24)$$

$$U = \operatorname{cosec} \theta \ M(i,x)/(M(j,x)) \quad (2-25)$$

$$V = 3.33 \times 10^5 (E_0^{1.65} - E_c(i)^{1.65}) \times (M(j,x)) \quad (2-26)$$

$$M(j,x) = \sum_{i=1}^{i=n} C(i) \times M(j,i) \quad (2-27)$$

$$M(i,x) = \sum_{j=1}^{j=n} C(j) \times M(i,j) \quad (2-28)$$

$w(j)$ is the fluorescence yield for element j and the rest of the terms have already been defined earlier in this section.

Table 1 lists the values of $w(j)$ for several elements C, O, Al, Si, S, Ca and Fe. Appendix I lists the values of Y_0 , Y_1 , Y_2 , U and V for four elements Al, Si, S and Ca. Iron is not included, because it does not meet the criteria outlined by equation (2-19) when it is analyzed in the presence of C, Al, Si, S or Ca. In a coal particle containing elements Al, Si, S, Ca and Fe, Al would need to be corrected for fluorescence by Si, S and Ca; Si would have to be corrected for S and Ca; sulfur for Ca and Fe and Ca for Fe only.

The last correction factor, fluorescence correction due to continuum x-rays, is generally small and can be ignored, as has been done in the present study. This factor has been discussed in detail by Hensen (58).

It is obvious from the discussion of the correction factors that these can be estimated only when the chemical composition of the particle is known. Since at the start of the analysis we do not have an estimate of the chemical composition, the correction factors are calculated by substituting the k ratios for their concentration in the equations. In this way rough estimates of factors can be made and rough concentration calculated from equation 2-4. Using these concentration values as the new k ratios and again calculating correction factors from these new concentrations, and so on until the results converge. However, this approach of iterations is time consuming, and it may take 5-20 iterations before convergence occurs. Instead a simpler approach proposed

by Ziebold et al (59) is widely used. In this approach rough correction factors are estimated only once using the original k ratios. From these correction factors, rough concentrations 'C' are calculated using equation 2-4. Then from the original k ratios and C, new values of k are computed by the following equation

$$k_{\text{new}} = \frac{k_{\text{prev}}(1-C)}{k(k_{\text{prev}}-C) + C(1-k_{\text{prev}})} \quad (2-29)$$

In the first iteration $k_{\text{prev}} = k$. Using these new values of k and k_{new} a new set of C values is computed by equation 2-4. These are again substituted in equation 2-29 with $k_{\text{prev}} = k_{\text{new}}$ and from this k(new) values are calculated and so on until $k(\text{new}) - k(\text{prev}) = 0$. Then either of the two values is the weight fraction of that element in the sample.

2.2.7. Implementation

This implementation of a scheme for actual analysis of coal particles was carried out under two tasks, sample preparation and software implementation. The hardware modifications were implemented by earlier workers which resulted in the development of the CESEMI system. The CESEMI system discussed in section 2.3.1 was used as such without any modifications.

2.2.8. Sample Preparation

Sample preparation involves two main steps for a particular coal sample. Sampling a small amount (a couple of grams) of coal particles from either a run-of-mine sample of 1000 kgm or a pulverized coal sample of 200-300 kgms from a power station and preparation of the sample for actual analysis.

ASTM standards D2234 and D2013 were followed for sampling coal particles from a run-of-mine coal sample. The flow sheet of the procedure is outlined in Figure 5.

Sampling from a pulverized sample is comparatively easy, in that the sample is reduced by repeated cone and quartering and then repeated riffing until a 10 gm sample is collected.

Though the samples could be prepared by either dispersing the samples on a suitable substrate or by preparing polished sections of coal particles embedded in a suitable resin, for actual analysis only polished samples were used in this study.

In the case of a polished sample there is some ambiguity in size reported for the particles. This may be understood by considering Figure 6, which shows a vertical section of the polished sample. The polished surface passes randomly through the bulk of the particles. The cut may expose the full diameter of the particles or just an edge of the particle, as shown in Figure 6. The size reported for the cross-section may not be the actual size of the particle. On the other hand, though dispersed samples do not have this problem, they pose the other problem of varying x-ray absorption paths as discussed under section 2.4.1. As a

SAMPLE COLLECTED , 900 kgm. ROM

Figure 5. Flow chart of sampling procedure.

Figure 6. Exposed sections of particles upon polishing.

result of this, varying x-ray intensities are reported for particles of identical composition studied under identical conditions. To get an estimate of the deviation between x-ray intensities from different particles of identical composition and different points on the same particle, several tests were run with polished and dispersed samples of pure particles of alumina, silica, kaolinite, hematite, iron pyrite and feldspar. The percentage deviation of 90% of the points on different particles from the mean is shown in Table 5. In the case of dispersed samples, the deviations are large except for hematite; in the latter it was observed that most of the dispersed particles were flat particles. Deviations from 25 to 37% are too high for the results to be useful and the approach of using dispersed samples was abandoned.

The ambiguity in the reported size on the polished sections was reduced by using fractions of narrow size ranges in preparing polished samples. During analysis, if the size of the cross-section falls within the size range of the particles originally present in the pellet, it is assumed to be a cross-section through the bulk of the original particle and is further analyzed, whereas smaller sizes are ignored, since they arise from a section through the edge of an original particle.

From the discussion in section 2.2, it is obvious that to use polished samples, the atomic number of the resin should be higher than the coal. A technique (60) has been developed for preparing a pellet of coal particles embedded in barium-containing resin. Attempts to use iron and cobalt instead of barium resulted

Table 5

% deviation from the mean

	<u>Mineral</u>	<u>Element</u>	<u>Polished Particle</u>	<u>Dispersed Particles</u>
1.	Pyrite	Fe	±6	±30
		S	±5	±30
2.	Feldspar	Si	±3	±30
		Al	±6	±34
3.	Kaolinite	Al	±11	±37
		Si	±11	±30
4.	Hematite	Fe	±3	±12
5.	Alumina	Al	±8	±25

x-ray collection time = 3 seconds

in poor quality pellets. It was possible to produce a good quality pellet with lead, but the x-ray energy of $M\alpha$ line of Pb is almost the same as that of $SK\alpha$ (2.31 kev) and so lead would interfere with sulfur analysis. The complete details of preparing polished sections of coal particles of narrow size ranges from a pulverized sample are given in Appendix II. Though dispersed samples of coal particles were not used for analysis, a technique to make dispersed samples was developed as part of this study, in order to give size distributions of the pulverized coals. Appendix III describes this method.

A computer program was written (61) to accomplish the task of analyzing several thousand particles using the CESEMI system hardware discussed in section 2.3.1. The program essentially makes the electron beam scan the polished surface of the coal-containing pellet. Using back-scattered electrons as the image producing signal, the beam recognizes the edge of the particle and traces around the perimeter of the particle. The perimeter points so generated are stored in a buffer of 10 K using two words to store the co-ordinates of one perimeter point. A line integral is performed on these x,y co-ordinates to get the size (area mean diameter) of the particle cross section. If the size of the cross-section falls within the original sieve size (as discussed earlier), it is further analyzed by collecting x-rays from various representative test spots on the particle. These spots are chosen by deducing the maximum number of circles 8 μ m diameter which can fit into the cross-section, to cover as much

of the cross-section of the particle for x-ray emission as possible. For large particles, eight evenly spaced circles are chosen as representative of the sample. The beam is brought to rest for two seconds at the center of each of these circles to generate characteristic x-rays. If the shape or size of the particle does not allow any 8 μm circle to be fitted, the center point of the particle is chosen as the test spot.

The x-rays are collected for only five elements, Al, Si, S, Ca and Fe. Oxides of these metals are major mineral constituents in coal. To estimate background, x-rays are collected in three channels set at the 1.32, 2.62 and 6.1 kev. The 1.32 K α line is used for correcting the x-ray counts for Al and Si, 2.62 K α line for Ca and S and 6.1 K α line for Fe. The x-ray counts for each of these eight channels (including background) are added for the various test spots on the particle and averaged. A correction procedure based on the ZAF procedure as described in section 2.4.1 is used to convert these average x-ray counts for each channel to weight percentages of mineral elements. A sixth element is estimated by difference and assumed to be carbon, which means all other elements (N, O, H, K, Na) are treated as C. The x-ray data on standards is collected manually for a specified time. The standards used are high purity crystals of alumina, quartz, calcite and iron pyrite.

Various modules of the program are interrupt-driven so as to obtain maximum overlap of data collection and analysis. During the time the beam is resting on the particle for collecting x-rays,

the computer is evaluating the size of the particles, computing future x-ray collection points and applying the ZAF correction procedure to obtain composition.

2.3. Description of the Computer Program

2.3.1. Introduction

A complete description of the computer program is presented in this chapter. The program has seven main modules. These are

- 1) Input routine
- 2) Search routine
- 3) Trace routine
- 4) Schedule routine
- 5) Size routine
- 6) X-ray sampling routine (point)
- 7) ZAF correction routine

These modules will be discussed under four headings:

- a) Algorithmic details, outlining the flow and logic of the program
- b) Memory and language details, discussing the memory requirements for each module and the language used in writing these modules
- c) Time details, outlining the analysis time of the program and
- d) Execution details outlining some possible problems during execution of program.

2.3.2. Algorithmic Details

The algorithmic details for various modules of the program are as follows:

2.3.3. Input Routine

This routine accepts input data such as magnification, x-ray counts from standards, x-ray collection time for standards, point density, and size range of the particles. No default parameters are provided within the program.

After the user has specified these inputs, it calls all the other routines and initializes the necessary variables supplied by the operator in each of these routines. It then calls the search routine.

2.3.4. Search Routine

The flow chart of the search routine is shown in Figure 7. It starts by moving the electron beam from the upper left hand corner of the grid ($x=0$, $y=0$) horizontally until it comes to the opposite frame edge ($x=4096$, $y=0$). It then moves the beam back to the left hand edge of the next line of scan and begins scanning this line. The process is continued until the beam reaches the lower right hand corner ($y=4096$ and $x=4096$) of the grid. At this stage the program calls a subroutine 'LPRT' (last particle) and finishes analysis of the last particle on the current frame. It then checks if the user is done with his specimen. If he is not the program is repeated.

Figure 7. Flow chart of search routine.

During scanning, the search routine checks the status of each point (STCHK) on which the beam is resting. If it detects an 'ON' point, it then checks whether the next five points of scan are also 'ON', to ensure that the current particle is at least of 1 μm in diameter. If the particle meets this criterion, it is traced by calling the trace routine, followed by calling the schedule routine. Both of these routines are discussed in the next section.

In its horizontal scan, the beam moves in a series of jumps from one point to another and the distance between two such points or the point density (PDN) is specified by the user as 1, 2, 4, 8 or 16. The electron beam spends 100 μsec at each point before moving to the next point. The reason for providing a relatively long time, 100 μsec at each point is due to the magnetic hysteresis of the scan coils of the microscope. It is the scan coils that control the movement of the beam. This is achieved by applying potential to the coils which in turn effects the magnetic field of the coils. Due to the hysteresis problem, the response of the magnetic field to the applied potential is not instantaneous, or in other words the response of the electron beam to control instructions that control the applied potential to the coils is not instantaneous. Thus the beam can be assumed to be at the particular location only when some finite time has elapsed after the control instructions have been specified by the computer. This time was experimentally found to be 100-250 μsec at an acceleration voltage of 20 kV and a point density of one.

2.3.5. Trace Routine

The flow chart of this routine is shown in Figure 8. It has basically four loops. The program always starts from loop one. Before entering loop one or any of the other loops, the program ensures that the beam is outside the particle. A point density of one is always maintained while in this routine.

In loop one the electron beam is moved inside the particle by incrementing the x-coordinates for a maximum of six points until the interface reports that the beam is inside the particle. It is then moved outside the particle by decrementing the same x-coordinates for a maximum of six points until the interface reports that the beam is outside the particle. At this stage, the beam is moved one step up by incrementing y and the process is again repeated. In this way the beam traces the upper left hand quadrant of the particle in Figure 10. However, it may happen during tracing that the beam does not find an 'ON' point as it moves in the positive x-direction (as in Figure 9) or it does not find an 'OFF' point as in Figure 9. In the former the program enters loop two and in the latter it enters loop four.

In loop two the electron beam is moved inside the particle by incrementing y for a maximum of six points until the interface reports that the electron beam is inside the particle. It is then moved outside the particle by decrementing y for a maximum of six points until the beam is reported to be outside the particle. At this stage the beam is moved to the right by incrementing x, and the process repeated. In this way the beam traces the

Figure 8(a). Flow chart of trace routine: Loop 1 and Loop 2.

Figure 8(b). Flow chart of trace routine: Loop 3 and Loop 4.

Figure 8(c). Flow chart of trace routine Kumar subroutine.

Figure 9. Beam movement in various loops.

← beam movement
 -.- particle boundary
 --- beam stuck

upper right hand quadrant of the particle in Figure 10. Again, as before, two conditions of not finding an 'ON' point or an 'OFF' point as shown in Figure 9 are handled by leaving loop two and entering loop three or loop one respectively.

In loop three, the beam is moved inside the particle by decrementing x and outside by incrementing x . While the beam is outside the particle, it is moved one step down by incrementing y , and the process repeated. In this way the lower right hand quadrant of a particle shown in Figure 10 is traced. As before, the two possibilities that may arise are shown in Figure 9. Such situations are handled by entering loop four or loop two as shown in the flow chart in Figure 8.

In loop four, the beam is moved inside the particle by decrementing y . At this stage, the beam is moved one step to the left by decrementing x and then the process repeated again. In this way the lower left hand quadrant of the particle in Figure 10 is traced. Again, the two possibilities that may arise while in this loop (shown in Figure 9) are handled by entering loop one or loop three.

The movement of the electron beam on an odd-shaped particle is shown in Figure 10. The program traces such a particle without too much difficulty.

From the flow sheet of the "Trace" routine, it can be seen that this routine calls a subroutine named "Kumar". The details of this routine are shown in Figure 8 itself. This subroutine

Figure 10. Movement of the electron beam on a) a spherical particle b) an odd shaped particle.

$\oplus$ Location on particle when program leaves a loop.

stores the current x and y coordinates of the beam. It may then call a couple of other subroutines, depending on the status of the indicated flags "FGR" and "FLAG". A discussion of the various subroutines is presented next.

The "GRLMT" (Grid limits) subroutine basically ensures that the values of x and y are between 0 and 4096, so that the beam remains within the grid boundaries. If, however, the values of any of the co-ordinates is either 0 or greater than 4095, it returns a flag "FGR" as true, indicating that the current particle is at a grid limit. Such a particle is not analyzed further and the buffer holding its x and y co-ordinates is cleared of its contents by calling the "ERASE" routine, which erases the buffer holding the perimeter points.

The "STORE" subroutine stores the x and y coordinates of perimeter points in a buffer of 10 k. Each of the coordinates is stored in one word of the memory. This routine maintains a pointer to the next available location for storing the coordinates of the next perimeter point.

The "LEAVE" subroutine essentially compares the current x and y coordinates of the particle with the coordinates of the first point, from where the trace routine began tracing the particle. If only y matches, then the x-coordinate is stored in as XPM. If both x and y match, that would mean that the perimeter of the particle has been completely traced and the beam has come back to the starting point. A "FLAG" is set to signal the trace routine, indicating completion and the beam is moved to $XPM + 4$

points before returning back to the search routine. The "LEAVE" subroutine calls another subroutine "CHECK" to ensure that the current particle was not traced before. This is done by checking whether the y-coordinate of the current perimeter point is on a previous line of scan. If it does the particle must have been traced before and is not analyzed further.

After the "TRACE" routine has traced a particle, the program returns back to "SEARCH" routine which calls "SCHEDULE" routine to schedule the sequence of various operations that need to be performed on the particle.

2.3.6. Schedule Routine

The flow chart of the "SCHEDULE" routine is shown in Figure 11. If the beam is on the first particle traced, the size routine is called first to find the size of the particle followed by the routine "POINT", which chooses the x-ray sampling points for the first particle. If the particle traced was the second particle, the subroutine "XRITA" is called to locate the beam on the first particle traced and to collect x-rays from the x-ray sampling points on that particle. It sets the interrupt and proceeds on to find size and x-ray sampling points for the second particle. After having finished with the calculations, the computer waits for the interrupt to signal the end of the collection of x-rays.

If the particle traced was the third particle, after locating the beam on the second particle, the ZAF correction procedure is applied to the data from the first particle, followed by printing

Figure 11. Flow sheet of the Shah (schedule) routine.

its size and compositions. The program then calls on the routines "SIZE" and "POINT" to find size and x-ray sampling points for the third particle. The process is repeated for the fourth particle and so on.

To handle the last particle traced, the subroutine "LPRT" is called from the search routine. This subroutine performs calculations on the last two particles. After having finished the slide this subroutine locates the beam on the last particle traced and applies the ZAF correction procedure on the previous particle and prints it. It then waits for the interrupt. Upon interrupt from the last particle, the ZAF correction procedure is performed on the x-rays for this particle and then printed.

2.3.7. Size Routine

This routine works on the buffer which contains the x,y coordinates of the perimeter points of the particle. This routine performs a line integral on the x,y coordinates to get the area of the particle. This area is reduced to an equivalent circular diameter which is returned to the schedule routine. The flow sheet of the size routine is shown in Figure 12. The basis for the diameter calculation is as below.

The width of the grid is $9/M$ cms., where M stands for the magnification used. Therefore one frame on the screen represents an area of $81/M^2$ square cms. Further, one frame is composed of 4096×4096 points, so that each square grid point represents an area of $\frac{81}{M^2 \times 4096 \times 4096}$ square cms or $483/M^2$ square micrometers. Let 'A' represent the area of the particle calculated by

A = Area
 PRPT = Number of
 parameter points
 MAG = Magnification
 DMTR = Diameter in μm .
 I = Index of x,y array

Figure 12. Flow sheet of Size routine.

performing a line integral on the x,y coordinate of the perimeter points. Then A represents an area of $483 \times A/M^2$ square microns. Letting D be the equivalent circular diameter of the particle.

$$\frac{\pi D^2}{4} = \frac{483 \times A}{M^2}$$

or

$$D = \sqrt{A} \times 24.79/M \quad (3-1)$$

2.3.8. Point Routine

This routine is used to find the x-ray sampling points for the particle that was traced. It uses the co-ordinates of the perimeter points as the input, to deduce the maximum number of circles of 8 μ m in diameter which can fit in the cross section. The flowsheet of the routine is shown in Figure 13; 'NXRY' represents the number of x-ray sampling points, which is initialized to zero. To understand the logic of this routine, consider Figure 14 also, in which the particle is outlined by thick boundaries. The 'POINT' routine first calls a subroutine 'YMIN' to find the minimum and maximum co-ordinates of the particle indicated by $Y_{\min}$ and $Y_{\max}$ in Figure 14. $Y_{\min}$ is stored in a location identified by Y_c . A new value of Y_c is computed by adding 'INCR' to the old Y_c . The value of 'INCR' depends on the magnification and is adjusted such that it corresponds to a distance of 4 μ m (half the diameter of the emission volume). It is computed by the equation

Figure 13. Flow chart of Point routine.

$$\text{INCR} = \frac{4096 \times M \times 4}{9 \times 10^4} = 0.2 M \quad (3-2)$$

The new value of Y_c is tested to see that it is at least INCR points above $Y_{\max}$. A negative answer would indicate that the particle is less than 8 μm in size along the Y-axis. 'NXRY' would be zero for this particle. For such a case subroutine YMCOMN is called again but this time it returns minimum and maximum x-coordinates of the particle indicated by $X_{\min}$ and $X_{\max}$. From this information the coordinates of the sampling point are computed. These are indicated by ' X_c ' and ' Y_c ' in Figure 13. It is further tested to check that the point lies on the particle. In case of a positive test, the coordinates of the point are stored to be used as a sampling point. A negative test would indicate that the particle is oddly shaped and is ignored for further consideration.

If the particle is greater than 8 μm in length along the Y-axis, a subroutine 'XRINT' is called which returns x-coordinates for points Y_1 and X_2 in Figure 14. The number of such points is stored in 'XEDGS'. Further 'INCR' is added to the minimum of the two x-coordinates (point X_1 in Figure 14) and this point is tested to check that it is at least INCR points away from the next higher x-coordinate, i.e., the x-coordinate of the point X_2 . If it is not, as in example shown, it is ignored for further consideration, a new value of Y_c is computed and this time subroutine XRINT returns x-coordinates of four points i.e. points X_3 , X_4 , X_5 and X_6 and

Figure 14. X-ray sampling points from A particle.

'XEDGS' is equal to four. It picks up the first pair, i.e., x-coordinates of points X_3 and X_4 and tests if they meet the criterion outlined above. As can be seen from Figure 14 they do not and so the next pair, i.e., x-coordinates of points X_5 and X_6 are chosen and tested. In the example shown these also do not meet the criterion and are hence rejected. The process is again repeated by computing a new value of Y_c and calling subroutine 'XRINT'. This time it returns X-coordinate of points X_7 , X_8 , X_9 and X_{10} and now both pair of points meet the criterion outlined above. In such a case another subroutine, 'RAINA' is called.

The flowsheet of subroutine 'RAINA' is shown in Figure 15. This subroutine first saves the least of the x-coordinates of the pair in X_c , i.e., the x-coordinates of point X_7 in Figure 14. It adds to it 'INCR' points to get the x-coordinate of point P_1 . It is obvious that point P_1 whose coordinates are given by X_c and Y_c is at least 4 μm away from the x-coordinate of the left-most edge (point X_7) and at least 4 μm away from the x-coordinate of the right-most edge of the particle (point X_8). The 'RAINA' routine then calls subroutine 'XRINT' which this time returns the y-coordinate of all those points whose x-coordinate is equal to X_c or in the case of the particle in Figure 14, it would return the y-coordinates of points Y_1 , Y_2 , Y_3 and Y_4 . The number of such points is stored in a location identified by 'YEDGS'. Next the y-coordinate of point P_1 , i.e., Y_c is tested to see that it lies within Y_1 and Y_2 . If it does not it is tested against

Figure 15. Flow sheet of subroutine Raina.

the next pair, i.e. Y_3 and Y_4 . In the particle in Figure 14, Y_c lies within Y_1 and Y_2 . For the point P_1 to be a sampling point, it should be at least $4 \mu\text{m}$ below the y-coordinate of its upper most edge (point Y_1) and at least $4 \mu\text{m}$ above the y-coordinate of its lower most edge (point Y_2). The point P_1 meets both the criteria and is chosen to be a sampling point. Similarly the point P_2 also meets these criteria and hence is chosen to be the sampling point. Next 'INCR' points are added twice to Y_c to obtain lines X_{11} and X_{12} and the procedure repeated. The 'POINT' routine calls mainly two subroutines, the 'YMXMN' and 'XRINT'.

The subroutine 'YMXMN' finds the maximum and minimum value of X or Y coordinate for a particle. It performs a 'Bubble Sort' on the perimeter buffer to get the desired information.

The subroutine 'XRINT' accepts either X_c or Y_c and a key 'FGL' as the input. For a given value of X_c and $FGL = 0$, it will search the perimeter points buffer and extract from it Y co-ordinates of all those points whose x-coordinate is equal to X_c . It stores the number of such points at an address identified by 'XEDGS'. Similarly for a given value of Y_c and $FGL = 1$, this subroutine will return x-coordinates of all those points whose Y-coordinate is equal to Y_c and store the number of such points in 'YEDGS'. The number of points (XEDGS or YEDGS) is generally two for a simple particle but could be more than two for odd-shaped particles. Before returning the Y-coordinates or X-coordinates, this subroutine calls another subroutine 'EDGE' to arrange the points in an ascending order.

The number of sampling points for a particle depends on its size and may exceed eight for bigger particles. Since a maximum of only eight points are considered for x-ray analysis for any particle, the extra points in the latter case are dropped randomly with the help of a "Random Number Generator".

2.3.9. ZAF Routine

This routine is used to convert x-ray counts to their weight percentages, using the ZAF procedure outlined in section 2.4.1. The program to perform this task was written with the following aspects in mind:

- 1) The PDP-11/20 minicomputer used during this study, does not have any hardware to perform multiplication, division, exponentiation, trigonometric or logarithmic operations. These operations are performed by a call for a suitable library function by the software.
- 2) This computer does not have a hardware package for performing floating point operations.

As a result of these limitations floating point operations, particularly involving exponentiation or trigonometric functions, as the ZAF correction procedure requires, would be done relatively slowly on this computer. So, during on line analysis, if the equations are used as such the whole analysis would be slowed down. Hence the program was written so that such operations were minimized. This objective was achieved by imposing the following restrictions on the analysis procedure:

- a) only five elements are analyzed, viz., Al, Si, Ca, Fe and S. A sixth element assumed to be carbon is estimated by difference. This means that all the other elements (N, O, H, Na, K) are treated as carbon.
- b) all the experiments are performed at one fixed acceleration voltage of 20 kv and take-off angle of 35°.
- c) the same standards were used during the entire study and,
- d) only K α x-ray lines were used for analysis.

The last three restrictions do not affect the quality of the analysis. It may however be argued that it would be desirable to analyze additional elements in coal, for example, Na, K, etc. Though the software can be modified to include a few more elements, the present hardware does not allow the analysis of these elements.

The standards used in this study were high purity single crystals of Al_2O_3 , SiO_2 , CaCO_3 and FeS_2 for elements Al, Si, Ca and Fe and sulfur, respectively. The x-ray data obtained from these standards were of the form; the number of x-ray counts for an element x from a pure compound xy. But the ZAF method needs x-ray counts for x from pure x and not compound xy. This is obtained by the following equation

$$\frac{C(x,xy)}{C(x,x)} = \frac{I(x,xy)}{I(x,x)} \cdot k(A) \cdot k(A) \cdot k(F)$$

or

$$I(x,x) = \frac{I(x,xy)}{C(x,xy)} \cdot k(A) \cdot k(Z) \cdot k(F) \quad (3-3)$$

where $I(x,x)$ and $I(x,xy)$ stand for the x-ray intensity of x from its pure element x and compound xy , respectively. $C(x,x)$ and $C(x,xy)$ stand for weight fractions of x in pure elemental form x and compound xy respectively. Note that $C(x,x) = 1$. For a particular standard, $C(x,xy)$ is fixed, $k(A)$, $k(Z)$ and $k(F)$ would also be fixed under the conditions outlined above. As a result the ZAF procedure computed $I(x,x)$ from a simpler series of equations of the form:

$$I(\text{Al}, \text{Al}) = 2.3454 I(\text{Al}, \text{Al}_2\text{O}_3) \quad (3-4)$$

$$I(\text{Si}, \text{Si}) = 2.4951 I(\text{Si}, \text{SiO}_2) \quad (3-5)$$

$$I(\text{S}, \text{S}) = 2.4243 I(\text{S}, \text{FeS}_2) \quad (3-6)$$

$$I(\text{Ca}, \text{Ca}) = 2.3513 I(\text{Ca}, \text{CaCO}_3) \quad (3-7)$$

$$I(\text{Fe}, \text{Fe}) = 2.084 I(\text{Fe}, \text{FeS}_2) \quad (3-8)$$

The $I(x,x)$ values are computed only once in the program and that is at the time of calling this routine from the Input routine.

The ZAF routine is called out every time a particle is traced (except the first particle) and the calling routine (Schedule routine) supplies it with a buffer containing x-ray intensities from the eight channels. The eight channels correspond to aluminum, silica, sulfur, calcium, iron and three backgrounds. The program corrects the x-ray intensities for each channel for detector dead time as:

$$N = N' / (1 - N'T) \quad (3-9)$$

where N is the true count rate, N' is the observed count rate and T is the detector dead time. The value of T is specified to be 1 μ sec. The x-ray intensities are then corrected for background by subtracting the background counts from each of the channels and from these corrected intensities, k ratios for each element are computed. The k ratio of the sixth element assumed to be carbon is calculated by subtracting the k ratios of all the five elements from unity. Then correction factors are computed for each of the five elements, starting with Fe followed by Ca, S, Si and Al. Correction factors for C are not computed, though its k ratio is used in estimating the correction factors for the other five elements.

The various correction factors are estimated as follows:

- a) Atomic number: the program computes B and S factors separately. The B factors are computed using equation (2-6). The $BB(i,j)$ values needed for this computation are not calculated by the routine, but were calculated separately. These are listed in Table 3. Using the values in Table 3, the ZAF routine computes the $B(i)$ factor for element i by an equation of the form:

$$B(i) = k(Al)BB(i,Al) + k(Si)BB(i,Si) + k(S)BB(i,S) \\ + k(Ca)BB(i,Ca) + k(Fe)BB(i,Fe) + k(C)BB(i,C) \quad (3-10)$$

For each of the five elements analyzed, there is just one equation like 3-10 to calculate the back-scatter factor. The $BB(i,j)$ values need not be stored but are

used as constants in the equation 3-10. The S values are computed in exactly the same way using equation 2-12 and $ss(i,j)$ values from Table 4. In this way all the parameters for atomic number correction for an element are computed from two linear equations. B and S values for a standard are constant and are not computed. The value $k(z)$ is estimated by equation 2-5.

- b) Absorption Correction: The program computes $X(i)$ for an element using equation 2-17. The $M(i,j)$ values needed for the equation are given in Table 2. From the $X(i)$ values the absorption coefficient is computed for an equation of the form

$$\frac{1}{\Lambda(i)} = (1+a(i) \times X(i))(1+a(i) \times X(i)) \quad (3-11)$$

where

$$a(i) = 1.2 \times 10^{-6} \times (E_o^{1.65} - E_c^{1.65}(i)) \quad (3-12)$$

and will be constant for an element i and is not computed by the program but has been computed separately and used in equation 3-11. The absorption coefficient for a standard is a fixed quantity and is not computed. The value of $k(A)$ is then computed from equation 2-15.

- c) Fluorescence correction: The parameters needed for this correction are listed in Appendix 1. To apply this correction for an element i , only Y_2 , Y_3 and mass attenuation

coefficients of both the emitter and absorber in the specimen need to be computed. Y_3 is computed by equation 2-24 using the U and V values from Appendix I. Mass attenuation coefficients are computed from equations 2-27 and 2-28 using $M(i,j)$ values from Table 2. Y_2 is computed from mass attenuation coefficients using equation 2-23. The equations performing fluorescence correction (2-21 to 2-28) would ordinarily take quite some time in our computer, but using the parameters from Appendix I and putting them in simple linear equations, the operation has been simplified. The fluorescence factor is computed from equations 2-18(a) and 2-20. The fluorescence factor is unity for a standard. The value of $k(F)$ is then computed from equation 2-18.

The flow sheet of the program is shown in Figure 16. After the correction factors are computed for each element the concentration of each element is calculated from equation 2-4 and new k ratios are found by equation 2-29. In all, a maximum of four iterations are performed to obtain the corrected weight fractions.

2.3.10. Memory and Language Details

The complete program occupies about 18 K of the memory. This includes a buffer of 10 K for storing perimeter points. The remaining 8 K are occupied by various modules of the program. The trace routine, the largest of all the routines occupies about 4 K

Figure 16. Flow chart of ZAF routine.

of memory. The x-ray sampling routine occupies 2.0 K of the memory and the schedule routine occupies about 0.5 K. The search routine occupies about 0.25 K. All these routines are written in machine language, Macro-11, specified by Digital Equipment Corporation for the PDP-11 series of computers. Writing these routines in machine language makes the programs run faster and more efficiently. Of the other routines, both the ZAF and the size routine, which involve floating point operations and are difficult to execute in machine language, were written in Fortran. These occupy about 1.5 K of the memory. The input routine is also written in Fortran and occupies about 0.2 K of the core.

2.3.11. Time Details

Considerable reduction in analysis time is made possible because various modules of the program are interrupt driven, so as to obtain maximum overlap of data collection and analysis. During the time the beam is resting on the particle and collecting x-rays, the computer is running the ZAF, the Point and the Size routines. As a result the total time for analyzing a particle is approximately equal to the total x-ray collection time for that particle plus the time for tracing it. The time to analyze a particle is given by the expression:

$$\begin{aligned} \text{Analyzing time (seconds)} &= 2(\text{number of sampling points}) \\ &+ \text{Tracing time (seconds)} \quad (3-13) \end{aligned}$$

The first term on the right hand side results because the beam spends two seconds on each sampling point. The number of sampling points depends on size, so a larger sized particle will take more time to analyze. Tracing time depends on the size and shape of the particle, magnification and the quality of the back-scatter signal. Larger sized particles mean a greater perimeter to trace and hence greater tracing time. For a similar reason, particles with shapes closer to a circle lead to a shorter tracing time. Similarly a particle of a certain size analyzed at higher magnification would lead to longer tracing times. A noisy signal also makes tracing difficult and longer tracing times.

Figure 3-11 shows a plot of the analysis time for spherical particles as a function of the size at a magnification of 100x. The analysis time has been theoretically computed, assuming that the beam spends approximately 200 micro-seconds on each point before checking its status. In the same figure is included the x-ray collection time component of the curve, indicated by dotted lines. The x-ray collection time is constant for particles above 40 μm . This is because a maximum of 8 sampling points is allowed for any sized particle and this maximum is reached for 40 μm sized spherical particle.

It is obvious from the figure that the bulk of the time is spent in collecting x-rays. In fact for particles up to 75 μm sizes, 90% of the total time is spent in collecting x-rays. Thus, any improvement in tracing time is not going to affect the overall analysis time. As a result the curve in Figure 17 would be true

Figure 17. Analysis time as a function of the particle size, at a magnification of 100x. Dotted line indicates x-ray collection time.

for any image analysis technique using x-rays for chemical analysis.

2.3.12. Execution Details

The program has been run on a large variety of particles and in all cases, there were no tracing difficulties. It was run to estimate micro blow holes in a stainless steel casting and satisfactory results were obtained. It was also run on a polished ceramic pellet to analyze iron-rich crystals in it. The compositions predicted were found to be reasonable. The program also worked satisfactorily with medium and high rank coals. The data on coal particles is presented in Chapter V.

Lignite, however, led to some problems mainly because it was very difficult to obtain a well polished pellet. The pellet showed considerable relief on polishing and most of the particles showed a high degree of fracture. Since the program cannot identify fracture planes in a particle from its boundaries, fractured particles were treated as if they were composed of multiple particles. It is possible for the beam to get trapped inside the particle for ever. This, however, does not reflect any inherent weakness of the software, because these problems can be taken care of by devising a suitable sample preparation technique for soft materials like lignites.

It has also been observed that at times the beam gets trapped on a particle. There could be a variety of reasons for this, such as a poorly polished sample, an unclean polished surface, drift of the electron beam, vibrations caused within the specimen etc.,

but generally the frequency of occurrence of such an event is very low particularly with a good quality back-scatter signal. In any case, such a situation is handled by the program by generating an interrupt after the electron beam has spent more than five seconds tracing a particle. Upon receipt of an interrupt, the beam is taken out of the particle and the particle is discarded from any further consideration. The program, however, does print a message to the user about such a failure.

2.4. Sticking Apparatus Design and Characterization

2.4.1. Introduction

A system to study the wetting and sticking behavior of coal ashes and synthetic ash mixtures was developed, tested and modified.

The special features of this system include:

- 1) a pellet of ash can be melted very rapidly (heating rates above $400^{\circ}\text{C}/\text{sec}$) and brought in contact with a relatively cold metal substrate
- 2) the wetting behavior of this molten droplet with respect to the metal substrate can be measured in terms of the apparent contact angle of the droplet.
- 3) the sticking behavior of the droplet can be estimated in terms of the force needed to shear the droplet from the metal substrate
- 4) the metal surface temperature can be controlled anywhere from room temperature to 700°C , and
- 5) the substrates are replaceable, so that these can be chosen from any metal and may be independently subjected to any pretreatment.

The design of the system has been constantly improved with modifications since its day of inception and the discussion that follows refers to its most recent version.

2.4.2. Experimental Apparatus

The system has three main components

- i) a furnace to melt the pellet and control the temperature of metal substrate
- ii) a shear tester for measuring shear force between the ash droplet and substrate
- iii) an optical system to measure contact angle of the ash droplet with the metal substrate.

The furnace used is shown in Figure 18. The pellet of ash formed at the end of platinum wire is suspended by a pair of steel tongs in an alumina tube having three equispaced 15 mm slots to introduce three oxygen-methane flames to heat the pellet. A three-nozzle ring burner system shown in Figure 19 is used to produce the three flames. The alumina tube is mounted on a stainless steel cap which is in turn bolted to the transite top of an electric heating furnace used to control the temperature of the test substrate.

The bottom heating furnace consists of a cylindrical stainless steel shell 100 mm high and 200 mm diameter with top and bottom transite disks 10 mm thick. The heating element is wound round a centrally located alumina tube of 25 mm internal diameter and 3 mm thick which contains a stainless steel cylinder 22 mm diameter to conduct heat to the test substrate. The top of this cylinder has a cut of 25 mm x 19 mm and 5 mm deep to contain a rectangular substrate. The steel cap connecting the melting furnace with the substrate furnace has a central top hole which

Figure 18. Illustration of melting furnace mounted on substrate furnace.

Figure 19. Illustration of three-nozzle ring burner system.

allows the molten droplet falling off the platinum wire to strike the substrate after a fall of 35-45 mm. This cap also contains holes in the side to allow the droplet substrate contact to be viewed, to pass a thermocouple wire to a 2 mm diameter hole drilled in the substrate and to admit gas to control the atmosphere around the substrate and pellet if necessary. The substrate furnace has a 40V, 10 ampere variable power supply so that the substrate holding cylinder can be heated.

The connected furnaces are mounted on a hinge at the base which is, in turn, attached to a steel base plate with levelling screws. The hinge enables the system to be tipped so that the horizontal substrate with the attached frozen slag droplet is put into a vertical position. A hole in the side of the stainless cap is then directly under the droplet substrate interface, which enables the stainless rod of the shear tester to be pushed against the droplet.

The substrate consists of a rectangular metal piece (25 mm x 19 mm x 6 mm) into which is cut a slot of 25 mm x 14 mm x 4 mm to receive a rectangular platinum - 40% rhodium heater (30 mm x 12 mm x 4 mm) cast in alumina cement. The substrate along with the heater is mounted in the stainless steel cylinder through four allen screws. The platinum-rhodium heater has a 20V, 7.5 ampere variable power supply so that the temperature of the substrate can be accurately controlled up to 700°C.

The apparatus used as shear tester is shown in Figure 20. The figure shows the mounting of the ram to replace the pan of a

Figure 20. Arrangement for measuring adhesion force.

top loading balance with the balance resting on the platform of a hydraulic jack (12 ton capacity supplied by Walker Manufacturing Company of Racine, Wisconsin). The ram is 14 mm diameter at the base with a 60 mm long tip of 3 mm diameter, and ram is raised 1 mm by one complete stroke of the jack handle.

The droplet on the substrate is viewed with a Cathetometer X-2 Measuring Meter (supplied by Titan Tool Company, Buffalo, New York) with a 200 mm focal length microscope and horizontal and vertical displacement measurement over a range of 250 mm with a least count of 0.025 mm.

2.4.3. Experimental Method

Pellets of ash are made in 4 mm diameter holes drilled in a steel plate of 5 mm thickness giving a pellet weight of 70-110 mgm. About 2 gms of synthetic ash or coal ash (ashed according to the ASTM standard ash test or low temperature ash) are mixed with 0.2 ml of water and two drops of 10% Polyvinyl alcohol solution to act as binder. The steel mold is sprayed with mold releasing agent (supplied by Miller Stephenson Chemical Company, Danbury, Connecticut) and the 20 holes in the mold filled with ash paste. A 20-30 mm long and 0.3 mm diameter platinum wire is inserted in each pellet and the filled mold dried in an oven at 120°C for one hour. After cooling, the pellets are gently removed from the mold. A pellet is hung by a pair of tongs in the test furnace to be directly above the substrate.

The upper furnace is heated by oxygen-methane flame until the pellet melts and falls onto the substrate. The drop solidifies immediately on contact. The height and base of the drop are measured to estimate the apparent contact angle by the following equation

$$\tan(\alpha/2) = 2h/b \quad (4-1)$$

where α is the contact angle, h is the height of the drop and b the diameter of the contact area. After measuring the dimensions of the drop, the arrangement is tipped, with the substrate furnace still at the controlled temperature. If the drop does not fall off, the ram of the adhesion tester is gently raised to contact the drop. The jack is raised slowly and the reading of the balance when the solid drop shears off is taken as the adhesion force. This measurement can be made with a possible accuracy of 0.4 gms.

It was found that the drops stick to a substrate only if the substrate was above a certain temperature fixed for a given composition of the pellet. This temperature has been referred (66) to as the sticking temperature, which would be the temperature at which the drop just sticks when the apparatus is tipped to the vertical position. Below this temperature, the drop will fall off on tipping. This temperature can be reproduced within $\pm 5^\circ\text{C}$.

2.4.4. Equipment Characterization

The system was characterized with respect to such operating variables as height of the drop fall, weight of the pellet, part-

icle size of the material of the pellet, and presence of carbon in the pellet. The pellets made from a mixture of powdered minerals were tested on a mild steel substrate. The mixture of powdered minerals was made of 37 weight percent CaO , 20.4% SiO_2 , 18.8% Al_2O_3 and 23.7% Fe_2O_3 . The particle size of the mixture was about 95% minus 75 microns. The pellets were melted in a methane-oxygen flame (oxygen rich) and allowed to fall a distance of 40 mm (except when the height of fall was chosen as a variable) on to a pre-oxidized mild steel substrate (preconditioned at $400 \pm 5^\circ\text{C}$ in air for 20 hours to develop an oxide layer). The substrate temperature was varied between room temperature and 600°C in intervals of $50\text{--}70^\circ\text{C}$. At each experimental temperature the following data were reported for the glassy slag drop: 1) substrate temperature when the drop made contact; 2) contact angle of the drop with the substrate; 3) whether or not the drop adhered to the substrate surface and 4) the force needed to detach the drop from the metal surface, if it in fact did stick.

A thermocouple in the pellet (melting point of pellet $\sim 500^\circ\text{C}$) indicated that it took about 3-5 seconds for the pellet to reach its melting point and an additional 5-10 seconds for the complete melting and falling. The drops fall off the wire at $150\text{--}250^\circ\text{C}$ above the liquidus temperature of the pellet, depending on the viscosity of the drop. A heat transfer estimation suggests that the loss of temperature of the drop as it falls is about 70°C before it touches the substrate. The temperature of the sub-

strate during melting, adhesion and strength testing was constant within $\pm 5^{\circ}\text{C}$. The contact area between the solidified drop and the substrate ranged from 0.08 to 0.13 cm^2 . For the drops sticking to a metal surface, it was found that the reproducibility of the detachment force was within about $\pm 4\%$ when the force was beyond 10 gm and $\pm 10\%$ when the force was less than 5 gms.

In the first test, a comparison was made between pellets made from the standard mixture and pellets made from the same mixture ground very fine in a mortar and pestle. The results are shown in Figure 21 which indicates virtually no effect of the particle size of the material making up the pellet. In the second test, the effect of the height of fall of the drop to the substrate was investigated by varying fall height from 33 mm to 68 mm. Figure 22 shows the results. There is no effect on adhesion force, but the contact angle decreases somewhat for the longer fall at lower temperatures. This probably implies that the temperature history of falling molten drops is not significant compared to the effect of the substrate temperature within the conditions studied here. In the third test, the wetting and sticking behavior of pellets of 80 mgs were compared with that of pellets of 105 mg. As shown in Figure 23, the results indicate that the larger pellets give a lower sticking temperature and higher adhesion force. The contact angle of the larger pellet shows lower values at low temperatures while it shows higher values at higher temperatures. This implies that the solidification process of a droplet upon contact with the substrate may play an important

Figure 21. Variation of contact angle and strength with particle fineness.

Figure 22. Variation of contact angle and strength with fall height.

Figure 23. Variation of contact angle and strength with weight of droplet, fall height = 33 mm.

role on the sticking behavior. An attempt was made to prepare larger and smaller pellets. However, too small pellets did not fall off the wire and too large pellets did not melt uniformly or adhere consistently to the substrate. In the last test, a comparison was made between pellets made from standard mixture and pellets made from the same mixture with 20% graphite. The results are shown in Figure 24 which indicates virtually no effect of the presence of carbon in the material making up the pellet.

In addition, it was found that there was an optimum ratio of methane and oxygen flow rates in the flame for uniform melting of the pellet. This ratio was found to be 0.9, indicating that it was methane-rich. As a consequence of this it was found difficult to study the role of flame temperature. The pellet was melted at the tip of the flames, where the temperature was found to be around 1750-1800°C.

Since the results from the apparatus are comparative, it was felt necessary to fix the experimental conditions for all future studies. The conditions were fixed as:

- a) weight of the droplet: 80 ± 5 mg
- b) height of fall of pellet ~ 45 mm
- c) oxygen flow rate ~ 950 ml/min
- d) methane flow rate ~ 875 ml/min
- e) temperature of flame region where the pellet was heated $\sim 1770 \pm 20^\circ\text{C}$

Figure 24. Variation of contact angle and strength with and without graphite in the sample.

f) dimensions of the pellet 4 mm diameter and 4 mm
height

g) diameter of platinum wire holding the pellet 0.3 mm

In addition pellets were made under identical conditions.

2.5. Results

The results of the analysis of the coal particle are being published in two papers, copies of which appear in the rear pocket of this thesis. While paper I (67) discusses the results with the Keystone coal, the results of analysis with Comanche and Rosebud coal are discussed in paper II (68). Also included for convenience are two papers (III and IV) discussing the sample preparation (60) and analysis technique (61) for coal particles using CESEMI.

Results on the wetting and adhesion studies of synthetic and natural coal ashes have been discussed in paper V through X. Paper V (66) discusses the concept of sticking temperature and paper VI (67) discusses results with the ashes from four different coals. Papers VII (69), VIII (70), IX (71) and X (72) discuss the results with synthetic coal ashes.

Paper I. Elemental Analysis of Keystone Coal Particles

Paper II. Analysis of Pulverized Coal Particles (8 μm - 100 μm)
For Fe, S, Ca, Si, Al on a Particle-by-Particle Basis

Paper III. A Mounting Medium for Coal Particles

Paper IV. Inorganic Elemental Analysis of Coal Particles Using
Computer Evaluation of Scanning Electron Microscopy
Images

Paper V. Note: A New Test for Characterizing the Slag Deposition
Properties of a Coal Ash: The Sticking Temperature

Paper VI. The Sticking Temperature and Adhesion Force of Slag
Droplets from Four Coals on Mild Steel

Paper VII. Studies on Slag Formation in Pulverized Coal Combustors:
Part I. Results on the Wetting and Adherence of
Synthetic Coal Ash Drops on Steel

Paper VIII. Studies on Slag Formation in Pulverized Coal Combustors:
Part II. Results on the Wetting and Adherence of Synthetic
Ash Drops on Different Substrates

Paper IX. Studies on Slag Formation in Pulverized Coal Combustors:
Part III. A Preliminary Hypothesis for the Sticking
Behavior of Slag Drops on Steel

Paper X. Some Results of the Wetting and Adherence of Synthetic Coal
Ash Droplets on Steel

2.5.1. A Mounting Medium for Coal Particles

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A. K. Moza, D. W. Strickler and L. G. Austin, "A Mounting
Medium for Coal Particles", Scanning Electron Microscopy,
1978, Scanning Electron Microscopy, Inc., IL.

SEM, Mounting Medium, High Electron Density, Coal

Abstract

When coal particles are mounted in the usual embedding materials, the coal grains cannot be detected by either secondary electron or back-scattered electron imaging. Therefore, the coal particles cannot be located to do chemical analysis of the particles on a particle by particle basis. This has been solved by making a mounting medium for barium methacrylate so that the mounting medium has a much higher electron density than does the coal. The coal grains are easily recognized in the back-scattered electron image in polished sections.

Introduction

A rapid particle by particle analysis of coal dust could have wide applications in the field of coal research. Such an analysis could be useful, in studying the liberation of mineral matter in coal during grinding and in studying of deposits of slag formed in coal-fired electric utility boilers. The properties of a slag droplet formed in the combustion zone from a coal particle will depend on the mineral matter of the particular particle, rather than the mean mineral content of the coal. Medical studies of the effect of inhaled coal dust need to distinguish different types of particles in addition to the different sizes. Particle by particle analysis of coal might also be desirable in coal conversion processes like liquefaction and solvent refining because the catalytic reactivity of different particles will depend on the mineral present in them.

We are currently developing computerized SEM techniques for the particle by particle analysis of coal mounted in a medium and polished to a flat surface. However, a basic problem exists in this technique. All commonly used mounting media are essentially hydrocarbons; some, such as Spurr's¹, contain a small amount of chlorine and others, such as Paraplex², may contain a small amount of first row transition metals. All of these mounting media have electron densities approximately the same as coal. Therefore, coal grains cannot be recognized by either the BSE or SE signals. It would be desirable to have a mounting medium with an electron density less than coal, but no such medium is available. The next best solution is to develop a mounting medium with an electron density much greater than coal so that an inverted BSE signal can be used to recognize the coal grains. To this end, we have investigated polymeric media containing organo-metal additions.

One serious problem with this approach is that the x-ray energies of the heavy metals may interfere with those of the lighter elements which are of interest, i.e., Sk_{α} (2.31KeV) and PbM_{α} (2.34KeV). Several systems containing lead, iron or cobalt were tried but in addition to the interference problem, the composition did not harden. The best system found to date is based on barium methacrylate, which gave hard pellets suitable for polishing. Barium interfered with titanium, but

since titanium usually is not a major element in coals this is not a serious problem. The procedure for making this material is listed in Table 1. The centrifuge steps are essential to hold the number of gaseous bubbles to a minimum.

1. Dry coal in vacuum oven at 100°C and 100 torr for 1 hour.
2. Mix 6 g Paraplex 60², 6 g epoxy resin², and 4 gm. barium methacrylate.
3. Heat to 80-85°C for 1/2 hour.
4. Centrifuge to remove any undissolved barium methacrylate.
5. Add two drops cumene hydroperoxide and one drop cobalt activator². Mix thoroughly.
6. Add dried coal and stir to disperse.
7. Centrifuge one minute. Heat to 60°C for 5 minutes, centrifuge again. Put in vacuum oven at 50°C for 500 torr for 5 minutes.
8. Centrifuge two minutes. Harden at 45°C and 100 torr for two hours.

Table 1

Some typical micrographs of coal mounts made with this technique are shown in Figure 1.

Application

The coal powder was separated into closely sized fractions by wet sieving a water solution of 1% coal, 0.2% NPX Tergiton, 0.1% Calgon and 0.1% Dazad II KLS. Sieves of 90, 75, 60, 45, 30 and 20µm openings were used. From each size fraction (e.g. 90 x 75µm), a pellet was made using the procedure outlined in Table 1.

The polished pellets of coal were coated with carbon and analyzed using present single channel analyzers and an energy dispersive x-ray system. Only particles with a diameter within the sieve range were studied. The beam was placed at five different points on each particle and x-ray data collected at each point for five seconds. The five points were averaged to determine the composition of each particle. The weight percent of the elements were converted to oxides except for iron and sulfur. All of the iron was converted to pyrite with the excess sulfur being called organic sulfur. These results are presented in Table 2.

As expected the particle by particle analysis can be entirely different from the bulk analysis. There is some indication that pyrite

is concentrated in the smaller particles. With the very limited data available now, it is difficult to draw conclusions about the distribution of minerals in the coal grains. We are currently trying to scan the particles and do the analysis automatically, so that a large number of particles can be studied.

Acknowledgement

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References

1. Polysciences Inc., Warrington, PA
2. Tenneco Chemicals, Piscataway, NJ

Table 2

Example of Analysis of Coal Particles in the Polished Mounting Medium

Size Range of Particles in Pellet	Observed Size	Al ₂ O ₃	SiO ₂	FeS ₂	CaO	Misc.	Organic Sulfur	Coal by difference
69-75	70.0	12.9	11.3	22.3	0.9	N.D.	1.0	52
	63.5	-	17.0	0.65	-	N.D.	1.35	81
45-60	57.0	-	-	-	9.0	N.D.	2.3	89
	50.0	19.5	26.5	-	4.8	N.D.	0.4	49
30-45	41.6	-	9.4	1.3	-	N.D.	1.2	88
	35.0	-	7.0	-	-	N.D.	3.05	90
	31.0	-	1.8	-	-	N.D.	1.4	97
20-30	29.8	-	-	-	-	N.D.	1.7	98
	23.3	22.2	30.0	21.5	-	N.D.	0.3	53
0-20	18.5	11.2	13.7	17.6	-	N.D.	1.6	56
	12.8	-	-	41.6	0.5	N.D.	1.0	57
	10.2	-	-	-	-	N.D.	1.7	98
	9.5	-	6.7	18.9	-	N.D.	1.2	73
	8.0	2.0	1.5	-	-	N.D.	0.8	96
Bulk analysis as determined by Spectro- chemical analy- sis		5.35	11.4	1.45	0.6	1.2	1.5	78.5

1a

1b

Paraplex Mount

1c

1d

Barium Methacrylate Mount

Figure 1. SEM micrographs of coal particles mounted in Paraplex (1a SEI, 1b BSE) and barium methacrylate mounting media (1c SEI, 1d BSE).

2.5.2. Inorganic Element Analysis of Coal Particles Using Computer
Evaluation of Scanning Electron Microscopy Images

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Abstract

A new computer-controlled technique has been used on sieved coal powder mounted in a barium-containing resin to give a relatively fast analysis of particle size and mineral element composition. This new programming approach is modeled after the computer evaluation of SEM images technique developed at the Materials Research Laboratory of The Pennsylvania State University, but uses the interrupt mode of a PDP-11 to allow simultaneous tracing, x-ray collection and ZAF corrections, thus reducing the total time of analysis. The method used does not suffer from the previously encountered difficulties caused by included mineral matter or difficulties of defining the particle boundaries.

Introduction

As part of a project on the behavior of slag droplets formed from the mineral matter in particles of burning coal, we require a rapid approximate method for analysis of the inorganic elements in particles of coal of 5 μ m to 75 μ m diameter. The melting and adhesion behaviour of the droplet of glass formed from any given particle of coal will depend on the composition of minerals in the particle, and the usually determined mean values of inorganic ash composition for the whole coal are not relevant to the behavior of individual particles. It is likely that there are other cases where it would be valuable to characterize a coal powder as a matrix of different types of particles, with respect to appropriate size ranges and mineral composition ranges. These cases might include combustion, gasification, liquefaction, mine safety, etc.

To accomplish a rapid analysis of several hundred particles we are developing the CESEMI system of Libiedzik et al.¹ A computer-controlled beam is used to locate the size of a particle. The beam is located at suitable points on the particle, and x-ray fluorescence emissions are detected and analyzed in an energy-dispersive analyzer. This paper describes the procedure and logic steps for this procedure.

Sample preparation. A given coal sample is dispersed in water using a combination of dispersants which has been found² to be suitable for coal and coal-mineral composites. These are 0.3% Daxad (supplied by W. R. Grace and Co., Cambridge, Massachusetts), 0.2% Calgon (supplied by Calgon Corporation, Pittsburgh, PA) and 0.1% NPX (supplied by DOW Chemical, Co., Midland, Michigan) in water. The dispersed coal slurry is wet sieved through micromesh sieves (Buckbee Mears Co., St. Paul 1, Minnesota) to obtain closely sized fractions. For instance, a coal sample with a maximum sieve size of 75 μ m would be cut into size fractions of 75-60 μ m, 63-45 μ m, 45-30 μ m, 30-20 μ m, 20-10 μ m and 10-5 μ m. Each fraction is then dried in a vacuum oven at around 70°C for 30 minutes and a pellet of coal particles dispersed in barium-containing resin is prepared as described previously at the last symposium³. The pellets are polished in

the usual manner and the polished surface is coated with carbon for analysis.

Particle recognition and sizing. A back-scatter image of the coal particles in the barium-containing resin appears darker than the rest of the resin, because of the lower electron density of coal. Thus the back-scatter signal from the background is brighter than that from the coal and in some cases even brighter than the mineral matter. For using computer control, the EBS signal must be inverted to make the coal appear bright and the resin dark, but this will also make the mineral matter (higher atomic number than coal) in the particle look darker. This poses problems for conventional beam controls that scan the beam inside the particle. In such a case, the beam will report it has reached the edge of particle when it comes on a mineral grain within the coal particle. We have overcome this problem, by tracing the perimeter of each particle to define the particle before performing further calculations or x-ray testing.

A computer program has been written which makes the electron beam scan the polished surface of the coal-containing pellet. Using back-scattered electrons as the image-producing signal, the beam recognizes the edge of a particle and is made to trace around the perimeter of the particle. The movement of the beam is effected by electromagnetic hardware which does not respond instantaneously to control instructions, that is, the beam takes some time to reach a certain point. It is not feasible to allow a long period of time for each step, so the beam is taken to be at a particular point after about 100 microseconds and the computations started. Because the beam is not quite at the desired point, this has the effect of making the edge of the particle appear fuzzy to the computer, and somewhat variable depending on the direction of approach of the beam. The programming logic uses 3 steps (of a 4096x4096 grid) into the interior and 3 steps away as a definition of the particle edge. Thus, in tracing in the upper left hand quadrant the 6 steps left to right should report an average of 3 off and 3 on. If it reports 4 off, 2 on, the edge of the particle is moved one step to the left and the 6 steps repeated. The direction of scan is changed from left to right, to up and down, to right to left, to down and up, as the curvature of the edge changes. The perimeter points so generated are stored in a buffer of 10K, using two words to store the coordinates of one perimeter point. A line integral is performed on these x,y coordinates to get the size (mean area diameter) of the particle cross section.

If the size of cross section falls within the original sieve size range of the particles in the pellet, it is assumed to be a cross section through the bulk of an original particle and is further analyzed. Smaller sizes are ignored, since they arise from a section which is not passing through the center of an original particle and may, therefore, be only a small fragment. Since the x-ray test involves a pear-drop of sample volume below the surface of about 5 μ m diameter, it is necessary that the particle of coal be at least 5 μ m in depth and analysis of a small frag-

ment will not give valid answers.

After tracing the particle, x-rays are collected from various representative spots on the particle. The sample spots are chosen such that they cover as much of the cross section of the particle as possible. This is achieved through software by deducing the maximum number of circles of $8\mu\text{m}$ (or any other suitable diameter) diameter which can fit in the cross section, since $8\mu\text{m}$ is somewhat more than the excited x-ray emission volume for coal alone at an acceleration voltage of 20kV. For large particles, 8 evenly spaced circles are chosen as representative of the sample. The beam is made to rest for two seconds at the center of each of these circles to generate characteristic x-rays. If the shape or size of a particle does not allow any $8\mu\text{m}$ diameter circle to be fitted within the perimeter it is rejected.

The x-ray counts for each of six energy dispersive channels are added for the various test points on the particle and averaged. A correction procedure based on a modified ZAF method is used to convert these average x-ray counts for each channel to weight percentages of mineral elements. The various corrections used are described by Yakowitz et al.⁴ The x-rays are corrected for background and dead time before applying absorption, atomic number and fluorescence corrections. Fluorescence due to continuum x-rays is ignored, which is small compared to other inherent inaccuracies in the test. The modified ZAF computation procedure is sufficiently rapid that the computations can be performed while the beam is used to collect x-rays. Various terms used in the correction factors are stored in the program, because the number of such terms to be stored is feasible when only five elements are analyzed (Al, Si, S, Ca, Fe and C) at a fixed acceleration voltage of 20kV. The program determines carbon by difference, which means that all other elements (N, O, H, Na) are treated as C. Further reduction in computer time is obtained by avoiding more than four iterations and four iterations are preformed only when one of the correction factors is more than 1.2. It has been observed by us that if correction factors are small, it is not necessary to perform more than one iteration. The correction subroutine occupies about 0.5K of core.

The program is run on the PDP-11/20 computer, which is interfaced to the JOEL-SEM (model 50A). The program has five modules:

- 1) input routine, to accept input parameters of magnification, x-ray intensities on standards, size range of particles, etc.,
- 2) perimeter tracing routine,
- 3) line integral routine for calculating size of the particle,
- 4) x-ray sampling routine, to calculate points from which x-rays are to be collected,
- 5) ZAF routine, to perform ZAF corrections on the x-ray intensities.

The second routine is the largest, occupying about 15K of memory, including a buffer of 10K for storing x,y coordinates of perimeter points. The fourth routine occupies about 1K of memory. Both these routines are written in machine language. First, third and fifth routines involve floating point operations and are written in Fortran. These occupy about 1.5K of core.

All these modules are interrupt driven so as to obtain maximum overlap of data collection and analysis. The actual flow of the program is shown in Figure 1. After tracing the first particle, the computer performs a line integral on the particle and finds the x-ray sampling points. It then traces the second particle and after tracing it, the beam collects x-rays from the first particle, and the computer calculates the size and x-ray sampling point for the second particle. These calculations are rapid and after finishing, the computer waits for interrupt to signal the end of collection of x-rays. Upon interrupt the beam traces the third particle. After tracing the third particle, x-rays are collected from the second particle, while the computer performs the ZAF correction procedure on the x-rays of the first particle and upon completion prints its size and composition, and so on.

The total time taken for analyzing a particle is approximately equal to the total x-ray collection time for that particle plus time for tracing it, because the other computations are performed within the x-ray collection time. The tracing time depends on size of the particle and quality of backscatter signal. If the latter is noisy, more time is needed to trace a particle. On an average, tracing time for a particle of 50 microns at magnification of fifty is around 2-4 seconds.

Validation. To test the program, it was run on: (i) a dispersed sample of glass spheres of known size and (ii) polished sections of a mixture of pure particles of Al_2O_3 and CaCO_3 embedded in a resin. Glass spheres of 10-15 μm size were dispersed on a brass substrate using the method developed by Thanlow and White⁵. It was found that a count on about 100 particles gave about 89% of the particles in the certified size range of 10-15 μm and 97% of particles in the size range of 9-16 μm . Particles below 8 μm were particles broken during sample preparation. Particles higher than 16 μm are probably agglomerates.

High purity particles of alumina and calcite were dispersed in an ordinary organic resin and polished in the usual way. Tables 1 and 2 give typical data on the particles. As can be seen, the method analyzes around 49% of aluminum for alumina, whereas the true chemical analysis is about 53%. In the case of calcite, the amount of calcium reported is around 43% whereas it should be around 40%. The difference is probably because the program treats unanalyzed material as carbon and not oxygen. However we feel this level of accuracy is sufficient for our purposes.

To test our ZAF procedure, the same x-ray data was run through an existing complete ZAF correction procedure (MAGIC-IV) and our routine.

The weight percentage reported by the two programs showed a deviation of about $\pm 4.0\%$, which we feel is a satisfactory agreement.

Figure 2a shows a slide of coal particles and Figure 2b shows beam control on the same particles. Table 3 gives the data on coal particles. The data shown are not necessarily representative of a typical coal sample, but illustrate the kind of output that the test method produces.

There are, of course, other computer programs available for beam-controlled analysis. A complete paper would be necessary to give a listing of the publicly available programs, and a comparison is nearly impossible without field testing on a common sample. The authors are familiar with the work at The Pennsylvania State University, LeMont Scientific, and the Swedish work reported last year at this conference. It is the authors feeling that the procedure described in this paper is not available elsewhere. A paper presented last year at this conference by Lee et al.⁶ outlines a technique for mineral characterization in coal using combined Mossbauer-SEM studies. However, the technique is not suitable for the analysis of a large number of small particles.

This work was performed under Contract EF-76-S-01-2316, U.S.A. Department of Energy, and the program will be fully reported and thus available through the National Technical Information Service, Springfield, Va.

Acknowledgements

Authors wish to thank Mr. R. L. Myklebust of NBS and Mr. D. Strickler, Mr. K. Shoji and M. S. Stern of Penn State University for their help in carrying out this work.

TABLE 1. Analysis of pure alumina particles

Particle size, μm	Aluminum wt. %
30.0	49
28.0	49
22.0	49
19.0	49
16.0	49
13.0	49
8.0	49

TABLE 2. Analysis of pure calcite particles

Particle size, μm	Calcium wt. %
63.0	44
38.0	44
30.0	44
26.0	44
26.0	44
11.0	43
9.0	43

TABLE 3. Analysis of coal particles chosen at random to illustrate the variability of inorganic constituents.

Particle size, μm	Al wt. %	Si wt. %	S wt. %	Ca wt. %	Fe wt. %	Rest wt. %
64.0	5.8	7.9	12.6	--	6.7	67.0
43.0	24.6	24.3	2.5	--	--	48.6
32.0	16.8	3.1	2.8	--	--	77.3
20.0	14.3	8.6	9.1	4.8	6.4	56.9
19.0	--	--	3.5	--	--	96.5
9.0	2.1	1.5	30.2	2.1	23.95	40.3

Figure 1. Flowsheet of the program.

(a)

(b)

Figure 2. Backscattered electron image and beam control on coal particles

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Discussion with Reviewers

J. T. McCartney: Why was the size range 5-75 μ m chosen?

Authors: About 90% by weight of the coal particles burned in pulverized fuel fired boilers fall between 5-75 μ m.

J. T. McCartney: Why must the sample be analyzed in various size fractions? What proportion of a sample might be rejected and not analyzed less than 5 μ m? It would be a larger part of a respirable mine dust sample. If particles that cannot accommodate an 8 μ m circle are rejected, this would result in loss of even larger portions of a sample (Figure 3).

Authors: This technique is not suitable for particles less than 8 μ m in size because polishing small sized particles of a soft material like coal is very difficult and because the x-ray volume sampled might extend beyond the boundaries of the coal particle. To analyze respirable mine dust it is better to analyze dispersed samples of such particles rather than polished samples, but this will mean modifying the ZAF correction procedure and allowing for geometric factors.

J. T. McCartney: What would be the total time for a statistically satisfactory analysis of each size fraction? A whole sample?

Authors: The total analysis time for each size fraction depends on the size range of that fraction. The particles with higher size lead to larger x-ray collection times because of the higher number of sampling points on the particles. Generally 400-500 particles are analyzed from each fraction and total analysis time for pulverized coals burned in combustors would range from 8-10 hours.

Additional discussion with reviewers of the paper "Inorganic Element Analysis of Coal Particles Using Computer Evaluation of SEM images" by A.K. Moza et al, continued from page 476.

R. Raymond: You discuss your measurement and conversion to "weight percentages of mineral elements." In many cases, the analyses you make may determine elemental contents not present in a mineral phase, i.e., organic sulfur as seen in Table 3 where sulfur is present and iron is not. Are you attempting to program CESEMI to reduce the elemental data to specific mineral and non-mineral constituents?

Authors: Yes, we intend to reduce the elemental data to some specific minerals and the sulfur present in absence of iron would be treated as organic sulfur or a non-mineral constituent.

R. Raymond: As well as the average of various test points on a particle, it seems that the standard deviation of those analyses would enhance their use; three measurements made, for instance, on pure pyrite, kaolinite, and mineral free coal would give quite strange averages. Have you worked with the standard deviations of your average analyses to attempt correlating your elemental concentrations with mineral contents?

Authors: No, we have not at this stage but we will as our program to convert elemental data to some specific minerals is complete.

G. P. Huffman: If the center of the 8 μ m diameter circle is on or very close to a mineral particle, the excited x-ray emission volume will be only of order 1 or 2 μ m, depending on the type of mineral encountered. Is any correction made for this effect and, if not, what percentage error might this give rise to in the final chemical composition?

Authors: If the beam was directly on pyrite the sampled volume would be about 4 μ m diameter, but since this is smaller than the separation of sampling points this would cause no error.

G. P. Huffman: Is your software available to outside users at this time?

Authors: Yes it is available to outside users. However, since most of the software is executed in machine language, it may need some modifications before being used on another system with a different computer interfacing.

R. W. Stanton: What is the total time for a typical analysis of coal including all size fractions? How would the automatic analysis compare to a manually performed analysis timewise using an electron microprobe, for instance? How many particles must be counted for a representative analysis?

Authors: About 3000-4000 particles are needed to be counted for a representative analysis. To attempt to do this analysis manually, would take about 100-200 hours assuming that it takes the operator 2-3 minutes to position the beam on each particle, set the x-ray channels, compute size etc. The automatic analysis on the other hand would take 8-10 hours.

R. W. Stanton: To what top size is the sample pulverized? Is anything done with the less than 5 μ m coal or is the 10-5 μ m fraction in fact 10-0 μ m? Sieving particles less than 5 μ m is quite a feat.

Authors: The samples used in this study were not pulverized by us. These were supplied by Penn. Electric Co. of Pennsylvania. These samples were collected from the ducts that carry coal to the combustor. The present technique is not suitable for particles below 8 μ m.

R. W. Stanton: From table 3, it appears that you are in fact analyzing inorganic elements which may be either organic bound or in minerals. For instance, sulfur in the 32 μ m size particles: the sulfur is probably organic sulfur and not a mineral constituent.

Authors: The x-ray sampling will detect organic sulfur.

R. W. Stanton: Do these particle sizes range from 8-64 μ m? If so, what happened to your size fraction samples explained on page 2?

Authors: These particles range from 75 μ m and below. The data presented here are not typical data but illustrate the kind of output the program produces.

R. B. Finkelman: I think it unfortunate that the decision was made to speed up the analysis at the expense of Ti, P, and Cl, all major contributors to slag or indicators of slag forming potential. I, for one, would have opted to have fewer analyses but more complete chemical characterization of each particle.

Authors: We do not believe that Ti, P, or Cl contribute in a major way to slag formation. The one element that does would be Na but it is not possible to analyze it accurately with our present x-ray detection system.

R. B. Finkelman: Is a two-second analysis at 20kV sufficient to generate statistically significant number of counts?

Authors: For larger particles where counts from several points are combined, there are sufficient counts to get a good average. On smaller particles containing small amounts of mineral matter, the statistics of counting is not as good as we should like. We intend to extend the technique to a more modern instrument where the detected counts for this time can be increased by at least an order of magnitude.

2.5.3. Elemental Analysis of Upper Freeport Coal Particles

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For Presentation at the Annual SEM Meeting in Chicago, April 1980

Abstract

Over the past several years we have been studying the slagging properties of coal. New programs have been written for the computer-controlled SEM so that quantitative analysis of mineral elements in coal particles can be done automatically and quickly. The ZAF correction program has been modified so that Al, Si, S, Ca, and Fe are analyzed directly and the program assumes the balance of the material is carbon. Using this technique approximately 4000 coal particles (5 to 75 μm in diameter) have been analyzed. The elemental compositions have been converted to their respective oxides, and sulfur in excess of the organic sulfur has been converted to pyrite. These particles have been further grouped into five categories based on possible fouling characteristics. The coal tested was provided by the Keystone Power Company, Homer City, Pennsylvania, and was sampled from the ducts carrying the coal to the combustor.

Introduction

Slagging of heat exchangers in boilers is a very serious limitation on the operation of coal fired power plants. Many plants are forced to operate below design capacity to prevent fouling of the heat exchange surface. Since Pennsylvania produces a large quantity of coal and generates a large portion of electricity from coal, Penn State scientists have been studying the slagging problem for several years. Coal is fired into utility boiler furnaces as a fine pulverized powder suspended in air, and each coal particle burns as it moves along the coal-air flame. The mineral matter in each coal particle forms a droplet of fused ash, and some of these drops stick to the steel heat exchange surfaces and initiate the growth of a layer of fused ash on the surface. Analysis of the chemical composition of the mean coal ash only gives information on the melting point of the total ash mixture, whereas we feel that certain low melting point compositions occurring in a few of the particles may be the "bad actors" which initiate the slag growth.

To characterize a pulverized coal from this point of view it is necessary to estimate the different combinations of inorganic elements which occur in the thousands of pulverized coal particles. The technique we have been developing uses a computer-controlled SEM with x-ray fluorescence to estimate the major inorganic components in each particle.

Experimental Procedure

For this study a sample of Upper Freeport (Pennsylvania) E Seam coal was used. Using standard ASTM procedures the coal was sampled to get about 10 pounds of sample. This was further split to obtain samples for low temperature ashing (LTA), SEM and combustion studies. This final sample was subjected to a sieve analysis to determine the weight percent in the various size classes. Small amounts of samples for the SEM tests

were prepared by wet sieving using micromesh screens of 90, 75, 60, 45, 30 and 20 micrometers.

Each size fraction of coal was then mounted in a barium methacrylate mounting medium¹, polished and coated with a thin layer of carbon for analysis in the SEM. Using an inverted backscattered signal, the electron beam was made to trace around the perimeter of the coal grain to generate an array of x-y perimeter points on a 4096x4096 grid. The area of the exposed section of the particle was determined using a line integral and if this size was within the original sieve fraction the particle was further analyzed. This procedure assumes that if the exposed polished section is still of approximately the same diameter as the original particle then the section is passing through the bulk of the particle and is not just a small remnant of the original particle. For the 0x20 μm fraction only sections in the range 8 to 20 μm were selected.

The computer then uses the x-y points to calculate the position of touching 8 μm diameter circles which will fit into the exposed section. The center of these circles is used as a sampling point, x-ray data are collected on each of these points for two seconds and then counts averaged. The data is corrected for background and refined using an iterative ZAF program written specifically for coal^{2,3}.

The procedure ignores all coal particles less than 8 μm in diameter because the pear drop shaped x-ray sampling volume would extend beyond the coal for many of the coal pieces remaining after polishing, thus giving erroneous results. However, the fraction of the pulverized coal less than 8 μm in diameter is less than 4% by weight of the total. Further, the droplets of slag formed from the mineral matter in these small coal particles will usually be very small indeed and will leave the furnace in the gas flow.

Results

A complete chemical, organic phase and mineralogical analysis of the total coal sample is given in Tables 1 through 4. The chemical analysis was performed on a 750°C ash and the mineralogical analysis on an LTA sample. From x-ray diffraction and infrared analyses the minerals present were estimated and the quantitative mineral analysis is a correlation of the elemental analysis with the x-ray and infrared data.

The sieve size analysis is given in Table 5. About 60 weight percent of the grains fall in the size range of -45 +8 μm , which is a very convenient range for the SEM. Very large particles (> 100 μm) take a long time for the electron beam to trace and also have a large number of x-ray sampling points.

Table 1
Analysis of Keystone Coal

<u>Proximate Analysis</u>		
	<u>As rec'd</u>	<u>Dry</u>
% Moisture	2.00	xxxxxx
% Ash	19.60	20.00
% Volatile	28.37	28.95
% Fixed Carbon	50.03	51.05
	<u>100.00</u>	<u>100.00</u>
Btu	11885	12128
% Sulfur	1.44	1.47

<u>Ultimate Analysis</u>		
	<u>As rec'd</u>	<u>Dry</u>
Moisture	2.00	xxxxxx
Carbon	66.71	68.07
Hydrogen	4.25	4.34
Nitrogen	1.58	1.61
Chlorine	0.17	0.17
Sulfur	1.44	1.47
Ash	19.60	20.00
Oxygen (diff)	4.25	4.34
	<u>100.00</u>	<u>100.00</u>

Table 2
Keystone Coal: Inorganic Element Analysis of Ash

SiO ₂	56.9 %
Al ₂ O ₃	26.9
TiO ₂	1.28
Fe ₂ O ₃	7.90
MgO	1.18
CaO	1.58
MnO	0.024
Na ₂ O	0.36
K ₂ O	3.01
Ba	0.085
Total	<u>99.13%</u>

Table 3

Keystone Coal: Mineralogical Analysis

	<u>% of Mineral by Weight</u>
Quartz	18
Calcite	not detected
Pyrite	10
Gypsum	1-5
Kaolinite	28
Illite + Mixed Layer Clays	<u>~ 40</u>
	<u>~100%</u>

Table 4

Keystone Coal: Maceral Analysis

% Vitrinite	= 73.2
% Pseudovitrinite	= 12.4
% Semi-fusinite	= 4.1
% Fusinite	= 2.1
% Micrinite	= 3.8
% Exinite	= 3.5
% Resinite	= 0.1

Table 5

Size Analysis of Keystone Coal

<u>Size in Microns</u>	<u>Weight Percent</u>
-106 + 90	3.4
- 90 + 75	8.4
- 75 + 60	9.8
- 60 + 45	8.6
- 45 + 30	12.9
- 30 + 20	19.6
- 20 + 8*	33.7
-8*	3.6

* Estimated by Coulter Counter.

The number of particles analyzed in each size range by the SEM technique was roughly proportional to the weight percent of particles. This tends to give appropriate weight to the most abundant material. In all, approximately 4300 particles were analyzed. Each particle was analyzed for Al, Si, S, Ca and Fe while C was determined by difference. This is an oversimplification of the inorganic chemistry but it was necessary to reduce the time of analysis. Table 2 shows that these elements make up more than 95% of the ash.

After a coal grain has been analyzed the results are reported as weight percent of each element contained in the grain. Some typical results are given in Table 6. Since a total analysis is of more than 4000 particle grains it is cumbersome to report all of the results in this form.

The analyses were converted to oxides in the cases of Al and Si, Ca was converted to CaCO_3 , while the Fe and S were converted to Fe_2O_3 and FeS_2 . For particles which contained both Fe and S, the S in excess of organic sulfur (taken as 0.85% of coal) was converted to FeS_2 and any Fe that remained was converted to Fe_2O_3 . The sum of these minerals was reported as the weight percent of ash in the particular coal grain. The particles in each size range were then classified according to the percentage of ash contained in each particle. These results are shown in Table 7.

Next, the particles in each size range were grouped into five different types of particles according to their composition. Type I are particles containing less than 5% mineral matter, Types II and III contain FeS_2 and Fe_2O_3 , respectively, Types IV and V are the remaining particles with ash compositions indicating a liquidus temperature below 1550°C and greater than 1550°C , respectively. The decision between Type IV and Type V particles was made using the phase diagram for the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. For example, following the 1550°C liquidus isotherm, compositions with CaO greater than 60% and Al_2O_3 greater than 70% have a liquidus temperature greater than 1550°C . These data were incorporated into a computer program to determine the Type IV and V particles. The Types II and III were further subdivided according to the percentage of FeS_2 or Fe_2O_3 contained in the inorganic elements in each particle. The data on the various types of particles are summarized in Table 8.

Since the combustion temperature in a coal fired boiler is approximately 1550°C , it is assumed that the Type V particles probably do not contribute to slagging. Type I particles contain such a small amount of ash that the analyses are not reliable, and the ash is likely to break up during combustion of the particle, giving very small droplets.

It is difficult to derive liquidus temperatures for the Types II and III for lack of liquidus data in the $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ or $\text{CaO-FeS}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ systems. Limited conclusions may be drawn from the systems $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO}$ and $\text{Fe}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$. Compositions containing greater than 50%

Table 6

Analysis of Coal Particles Chosen at Random from Different Size Fractions

Particle Number	Particle Size μm	Number of Sampling Points	Al	Si	S	Ca	Fe	C by Difference
1	106	8	1.72	5.67	0.59	0.00	0.00	92.02
2	81	8	0.0	0.00	0.54	0.0	4.66	94.80
3	70	8	2.82	12.34	0.43	0.19	0.00	84.22
4	61	8	0.57	1.77	0.55	0.77	0.00	96.34
5	54	8	0.00	0.47	0.84	0.86	0.34	97.49
6	42	8	2.61	38.37	0.32	0.22	0.0	58.45
7	33	4	0.77	0.45	1.90	0.18	1.42	95.18

Table 7

Distribution of Total Mineral Matter in Keystone Coal Particles

Size Fraction	Number of Particles Actually Analyzed	% by number in size fraction of particles having mineral matter percentages							
		0-5	5-10	10-25	25-40	40-55	55-70	70-85	85-100
+ 90	204	49	26	11	5	3	4	2	-
-90 + 75	413	60	19	10	2	3	4	2	-
-75 + 60	459	53	24	12	2	3	3	1	1
-60 + 45	578	59	19	10	2	4	3	2	1
-45 + 30	653	60	14	9	2	5	5	3	2
-30 + 20	811	57	14	9	4	5	4	4	3
-20	1167	50	10	8	4	3	6	9	10
Total, % by wt. of total sample =	4285	53.6	14.5	9.1	3.9	4.2	4.3	5.6	4.8

Table 8

% By Number in Size Fraction of Different Types of Particles in Keystone Coal

Fraction	Type I	Type II (% FeS ₂ in Ash)					Type III (% Fe ₂ O ₃ in Ash)					Type IV	Type V
		0-5	5-10	10-25	25-50	50-100	0-5	5-10	10-25	25-50	50-100		
+ 90	7	4	1	2	-	2	8	-	-	-	-	9	67
-90 +75	12	7	2	1	2	2	5	1	-	-	-	12	56
-75 +60	10	4	3	3	3	1	4	1	1	-	-	8	62
-60 +45	12	7	4	5	2	1	5	1	1	-	-	8	55
-45 +30	13	5	6	4	3	2	3	1	1	1	-	7	54
-30 +20	8	2	7	2	4	3	5	1	1	1	-	8	52
-20 +8	7	5	4	6	8	6	11	3	2	1	1	5	41
<u>% by weight of coal</u>													
% by wt. of total particles = 9.0		4.5	4.4	5.1	5.0	4.2	6.9	1.7	1.3	0.7	0.4	7.0	49.8
<u>% by weight of ash</u>													
	0.5	0.4	0.5	1.2	2.2	2.8	0.6	0.5	1.2	0.1	0.1	4.5	84.5

Fe_2O_3 will have liquidus temperatures in the region of or below 1550°C , while the liquidus temperatures of compositions with less than 50% Fe_2O_3 will depend on the other constituents. In view of the low melting point of FeS_2 ($\sim 1190^\circ\text{C}$) the ash drops from particles containing FeS_2 should be sticky and contribute to slagging. In studies³ of melting of FeS in an oxidizing atmosphere for short time periods, 5 to 10 sec., we found that FeS_2 decomposed to FeS which also has a low melting point and would still give slagging problems.

We conclude that all Type II particles and Type III particles with greater than 50% Fe_2O_3 in the ash as well as all of the Type IV particles, might be sticky. From Table 8 one can conclude that this coal will contain approximately 23 weight percent of coal particles which give rise to sticky ash particles.

Summary and Conclusions

A method has been developed to analyze the inorganic elements of individual coal grains to aid in estimating the contribution of the ash of each particle to slagging of boilers. Particles containing 50% Fe_2O_3 or at least 25% pyrite tend to make sticky ash that may contribute to slagging. A systematic comparison of results to slagging behavior, for many coals, remains as a future task.

Acknowledgements

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2.5.4. Analysis of Pulverized Coal Particles ($8\mu\text{m}$ - $100\mu\text{m}$)
For Fe, S, Ca, Si, Al on a Particle-by-Particle
Basis

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Introduction

Of the approximately 3.5 billion metric tons of the coal mined over the world, about 60% is burned in pulverized form in utility boilers for electrical power generation. One of the major problems during combustion in these boilers is the formation of slag deposits on the heat transfer surfaces in the boiler. These slag deposits arise from the inorganic material that enters the furnace in association with coal. Accumulation of these deposits on the heat transfer surfaces leads to reduced output and altered flow patterns of combustion gases, causing derated operation or sometimes complete outages. In some cases, large masses of these deposits build up on the upper portions of a boiler furnace, break away, and on falling damage the lower portions of the boiler.

The importance of slag deposit formation may be gauged from the large amount of literature available on this subject. A considerable portion of the work done in this area has been to predict the slagging behaviour of a pulverized coal from the mean ash compositions of the whole coal. It has been attempted by various workers to correlate the slagging behaviour of a coal with such properties as viscosity of the coal ash^(1,2,3), temperature of critical viscosity^(4,5), fusion temperature⁽⁶⁾, etc. Empirical factors such as slagging factor⁽⁷⁾, fouling factor⁽⁷⁾, dolomite percentage⁽⁸⁾, ferric percentage⁽⁹⁾, and base-to-acid ratio⁽¹⁾, have been devised. These indices of slag behaviour are based on tests on the mean coal ash.

We tested these correlations and indices in a comparison of two coals, Comanche coal and Rosebud coal, supplied to us in pulverized form by the Combustion Engineering Co., Connecticut. According to pilot-scale and full-scale experience of Combustion Engineering, Rosebud coal had exhibited severe slagging tendencies as compared to low slagging tendencies for Comanche coal, when burned in identical units. The results of analyses of these coals are given in Tables 1-6. Comanche coal is a sub-bituminous C coal from the Roland seam, Gillette, Wyoming and Rosebud is a sub-bituminous B Coal, from the Rosebud seam, Rosebud County, Montana. The mineral analyses in Table 4 used the analytical methods⁽⁵⁾ of x-ray diffraction and IR spectroscopy.

Table 7 shows the comparison of the various slagging factors. The high base-to-acid ratio of Comanche (>0.5) would indicate slagging problems in comparison with Rosebud, as would the higher Na_2O content and the lower ash fusion temperatures in Table 2. Other factors are similar between the coals and ashes. However, Rosebud is the bad-acting coal.

The exact mechanism of the sticking of fly ash particles to relatively cold metal surfaces in the upper part of the furnace chamber is not known. In the convective heat transfer passes where the gas temperatures are lower, the fouling deposit is associated with a glue of condensed alkali pyrosulfates. However, the upper furnace slag deposits appear to grow from an initiating layer of fly ash particles which adhere to the surfaces. Whether the deposit grows to harmful proportions also depends on the rate of addition of further fly ash to the initiating layer, and

Table 1

Proximate and Ultimate Analysis of Coals Studied

	<u>Comanche Coal</u>	<u>Rosebud Coal</u>
a) Proximate	Wt. %	Wt. %
Moisture	14.8	11.3
Volatile Matter	38.6	34.7
Fixed Carbon	39.4	42.1
Ash	7.2	11.9
b) Ultimate	Wt. %	Wt. %
Moisture	14.8	11.3
Hydrogen	4.5	3.5
Carbon	58.4	58.1
Sulfur	0.8	0.7
Pyrite	0.2	0.1
Sulfate	0.1	0.1
Organic	0.5	0.5
Nitrogen	0.8	1.2
Oxygen	13.5	13.3
Ash	7.2	11.9

Table 2

Ash Fusion Test Analysis
(Supplied by Combustion Eng. Inc.)

	<u>Comanche</u> °K	<u>Rosebud</u> °K
Initial deformation temp.	1400	1450
Softening temp	1417	1477
Hemispherical temp.	1439	1500
Fluid temp.	1522	1610

Table 3
Chemical Analysis of ASTM High Temperature Ash

	Comanche Wt. %	Rosebud Wt. %
SiO ₂	31.6	46.8
Al ₂ O ₃	14.4	16.9
TiO ₂	0.97	0.81
Fe ₂ O ₃	5.85	6.59
MgO	3.09	3.28
CaO	19.6	9.16
MnO	0.064	0.112
Na ₂ O	1.37	0.46
K ₂ O	0.37	1.10
P ₂ O ₅	0.52	0.27
SO ₃	<u>22.5</u>	<u>9.8</u>
	<u>100.3%</u>	<u>95.3%</u>
	ppm	ppm
Ba	3600	5650
Be	4	6
Cr	85	75
Cu	210	150
Ni	160	130
Rb	35	50
Sr	2350	960
V	170	85
Zn	120	75
Zr	220	260
<hr/> Supplied by Combustion Eng. Inc.		
Water soluble Na	480	270
Water soluble K	120	130
Acid soluble Na	420	320
Acid soluble K	57	700

Table 4

Mineral Analysis of Low Temperature Ash
(N.D. = not detected)

	Comanche Wt. %	Rosebud Wt. %
Quartz	12	23
Kaolinite	30	37
Gypsum	48	21
Calcite	N.D.	1-5
Illite	N.D.	~10
Pyrite	3	4

Table 5
Maceral Analysis

	Comanche	Rosebud
Vitrinite	87.8	80.6
Pseudo Vitrinite	0.0	0.0
Fusinite	3.1	2.8
Semi-Fusinite	5.6	12.0
Massive Micrinite	0.5	0.6
Granular Micrinite	1.8	2.8
Exinite	0.9	1.1
Resinite	0.2	0.1
Alginite	0.0	0.0
Sclerotinite	0.1	0.0

Table 6

Sieve Analysis by Wet Sieving with
Micromesh Screens and Dispersants

Size micrometers	Comanche Wt. %	Rosebud Wt. %
-106 + 90	1.5	2.5
-90 + 75	15.1	11.2
-75 + 60	15.0	13.7
-60 + 45	13.4	14.4
-45 + 30	14.2	14.9
-30 + 20	10.2	11.3
-20	30.5	32
-8	4.2*	3.9*

* Estimated by Coulter Counter

Table 7

	<u>Comanche</u>	<u>Rosebud</u>
1) Type of Ash	lignitic	lignitic ^(8,9)
2) Temperature of critical viscosity, °K	a) 1550 b) 1425	1611 ⁽⁴⁾ 1693 ⁽⁵⁾
3) Viscosity, poise at 1700°K	15 17	180 ⁽¹⁰⁾ 178 ⁽⁵⁾
4) Base-to-acid ratio	0.65	0.32 ^(1,9)
5) Babcock and Wilcox slagging factor	0.34	0.23 ⁽⁷⁾
6) Calculated simple adiabatic flame temp. at 15% excess air, K°	1845	1797
7) Percent sodium oxide	1.37	0.46
8) Percent Alkalies (Na ₂ O+K ₂ O)	1.74	1.56
9) Babcock and Wilcox fouling factor	1.0	1.12 ⁽¹²⁾

the subsequent sintering to a strong mass. For this type of deposit problem, it is our opinion that attempts to predict the slag deposit behavior of a coal from the analysis performed on whole coal ash will meet limited success. This is based on the belief that the majority of coal particles in a combustor burn as individual particles, leading to individual ash particles. It is the interaction of these individual particles with the heat transfer surface which result in deposit formation. This interaction will depend on the range of compositions of these individual ash particles and there is no reason to believe that each composition will be the same as that determined by the average ash analysis based on the whole coal sample. In other words, it may be only a minor fraction of the ash particles which are "bad actors".

Therefore, to predict this slagging behavior of a coal it is desirable to determine the composition of a large number of individual ash particles resulting from burning the coal. Since it is difficult to obtain a representative sample of ash particles from a utility boiler for analysis, it is desirable to be able to perform mineral analysis on a representative sample of individual coal particles and then assume that each coal particle leads to ash particles with the same mineral composition as that in the original coal particle. The validity of this assumption will be discussed later on. A method developed at this university⁽¹¹⁾, CESEMI (Computer Evaluation of Scanning Electron Microscope Images), was modified to perform a relatively rapid elemental analysis of individual coal particles. In this paper, this method is discussed and applied to the two coals.

The CESEMI/x-ray fluorescence analysis technique

With the system developed by us using the CESEMI hardware, it is possible to analyze 4000-5000 coal particles of sizes ranging from 106 μ m to 8 μ m in diameter in about 10 hours. The analysis reports for each coal particle the mean projected area diameter and the weight percent of Si, Al, Ca, S and Fe. The confidence limits on these numbers are $\pm 10\%$. The method involves wet sieving⁽¹²⁾ a pulverized coal sample to obtain closely sized sieve fractions and making a test pellet from each of these fractions mixed with a barium-containing resin⁽¹³⁾. The pellets are polished, coated with carbon and analyzed. The software written to perform this analysis uses the inverted back-scatter signal as the image-producing signal and makes the electron beam trace around the perimeter of the coal particle, thereby generating x,y coordinates of the perimeter on a 4092x4096 grid. A line integral is performed on the x,y coordinates to compute the size of the particle cross section exposed in the polished surface. If the size of the cross-section falls within the original sieve size range of the particles in the pellet, it is assumed to be a cross-section through the bulk of an original particle and is further analyzed. Smaller sizes are ignored since they arise from a section which is not passing through the bulk of an original particle and may therefore be only a small fragment with a small thickness.

After tracing the particle, x-rays are collected from various representative spots on the particle. The sample spots are chosen such that they cover as much of the cross-section of the particle as possible. This is achieved through software by deducing the maximum number of touching circles of $8\mu\text{m}$ diameter which can fit in the cross-section. The representative spots are then chosen from the center coordinates of the circles, since $8\mu\text{m}$ is somewhat more than the excited x-ray emission volume for coal alone at an acceleration voltage of 20 KV. For large particles where the number of circles exceeds 8, a random number selector process is used to select no more than 8 sample points, to reduce analysis time. Particles smaller than $8\mu\text{m}$ cannot be analyzed since the excited x-ray volume would then extend into the resin. The beam is made to rest for two seconds on each sample point to generate characteristic x-rays. The x-ray counts for each element, after correcting for background and instrument dead time, are converted to weight percentages by comparing these x-ray intensities with the intensities from a standard and then applying corrections to account for differences in atomic number, absorption and fluorescence between the standard and coal particle. The correction procedure (referred to as a ZAF correction procedure) was written specifically for coal particles.

The programming approach uses the interrupt mode of the computer to allow maximum overlap of data collection from the SEM and data analysis by the computer, thereby reducing the analysis time to the minimum. A summary of the method may be found in a previous paper⁽¹²⁾ and complete details are given in the thesis by Moza⁽¹³⁾.

Experimental technique and data analysis results

Each pulverized coal sample was dispersed⁽¹⁴⁾ in a water solution containing 0.1% NPX-Tergaton (Union Carbide), 0.3% Daxad (W. R. Grace) and 0.2% Calgonite (Calgon). The dispersed coal slurry containing 4-5 percent of solids was sieved through micromesh sieves to obtain size fractions of $+90\mu\text{m}$, $-90+75\mu\text{m}$, $-75+60\mu\text{m}$, $-60+45\mu\text{m}$, $-45+30\mu\text{m}$, $-30+20\mu\text{m}$ and $-20\mu\text{m}$. Each fraction was dried in a vacuum oven at about 70°C for 30 minutes and used to prepare a test pellet. Pellets were made by heating 4 gms of solid barium methacrylate (Polyscience, Warrington, Pa.) in 6 gms of Paraplex G60 (Rohm & Haas) and 6 gms of APCO 5823 (Applied Plastic Co., El Segundo, Ca.) to dissolve as much of the barium methacrylate as possible, followed by centrifuging the mixture to remove undissolved barium methacrylate. Eight to ten drops of DRM-Cobalt 6 activation (Tenneco chemicals, Piscataway, NJ) were added to the mixture plus four to six drops of cumene hydroperoxide (Polyscience). At this stage coal was added and the suspension thoroughly mixed. The mixture of coal-resin slurry was poured into a bottle, which was alternately centrifuged and subjected to a vacuum of 100 torr for about 15 minutes. The pellet was finally allowed to harden for 4 to 5 hours in a vacuum oven at 100 to 150 torr at about 50°C . Upon hardening, the bottle was broken and the coal pellet sectioned normal to the base, polished and coated with carbon for SEM analysis.

At least 250 particles were analyzed for each size fraction. The actual number was roughly estimated from the weight size fraction in the coal and the mean particle size. A sample of the data is given in Table 8. This data is, of course, not statistically representative of a typical coal but it illustrates the format of the analysis. Since about 4000 particles were analyzed for each coal sample, it is impossible to present data for all the particles in the form presented in Table 8. Instead the data within a size range was grouped into different categories as follows.

The weight percents of Si, Al, and Ca were converted to equivalent weight percent of SiO_2 , Al_2O_3 , and CaCO_3 . In the case where a particle had no iron, FeS_2 and Fe_2O_3 were reported to be zero for this particle. However, if the particle did contain Fe, the sulfur in excess of the mean organic sulfur (computed by chemical analysis) was combined with Fe as FeS_2 and excess Fe converted to equivalent weight percentage of Fe_2O_3 . The sum of these computed weight percentages of SiO_2 , Al_2O_3 , CaCO_3 , Fe_2O_3 and FeS_2 was referred to as the percent mineral matter in the coal particle. Based on the amount of this mineral matter, particles were classified in groups of increasing mineral matter content. Tables 9 and 10 list such groups for each size range for Comanche and Rosebud coal. The row marked "Total" was computed by multiplying each element in a column with the fractional weight of that size range in the coal from Table 6 and then adding each column, thus giving an estimate of the fractional mass of the coal (larger than $8\mu\text{m}$) which contains a given range of mineral content.

The particles in each size range were then grouped into five different types. Type I is made up of those particles containing estimated mineral matter less than 0.5%. For the rest of the types, CaCO_3 was converted to equivalent CaO and the computed mineral constituents, namely Al_2O_3 , SiO_2 , CaO , FeS_2 and Fe_2O_3 , were normalized to a base of 100. Types II and III refer to particles containing FeS_2 and Fe_2O_3 respectively. Within Types II and III there was further subdivision depending on the weight percent of FeS_2 and Fe_2O_3 in the total ash in the particle. Types IV and V are those particles whose mineral matter corresponds to liquidus temperature less than 1550°C and greater than 1550°C respectively. The computation uses the phase diagram for the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (15). Following the compositions on the liquidus line of 1550°C , it is possible to deduce logical statements as to whether a certain composition has liquidus temperature above or below 1550°C . For instance, compositions containing CaO greater than 50% by weight or Al_2O_3 greater than 70% have liquidus temperatures greater than 1550°C . In this way, a total of 43 logical statements were used to describe the whole phase diagram. These logical statements were incorporated in a computer program that applied them to a particular particle composition to decide whether it was Type IV or V. Finally, in addition to reporting the estimated total ($>8\mu\text{m}$) mass fraction of coal containing a particular Type of mineral composition, the calculations were also performed to express the fraction of the total mineral content (in coal above $8\mu\text{m}$ in size) occurring as each Type.

Table 8

Estimated Composition of Coal Particles Chosen
at Random from Different Size Fractions

Particle number	Particle size μm	Number of sampling points	Al	Si	Wt.% S	Ca	Fe	Rest
1	106	8	1.7	5.7	0.6	0.0	0.0	92
2	81	8	0.0	0.0	0.5	0.0	4.7	94.8
3	70	8	2.8	12.3	0.4	0.19	0.0	84.2
4	61	8	0.6	1.8	0.5(5)	0.77	0.0	96.3
5	54	8	0.0	0.5	0.8	0.86	0.3	97.5
6	42	8	2.6	38	0.3	0.22	0.0	58.5
7	33	4	0.8	0.4(5)	1.9	0.28	1.4	95.2
8	16	2	1.1(5)	6.3	0.5	0.0	7.7	89.4
9	10	1	0.0	1.1	38	0.0	42	17.7
10	8	1	1.9	2.6	1.1	1.42	0.7	92.3

Table 9

Distribution of Estimated Total Mineral Matter in Comanche Coal

Size fraction μm	Number of particles analyzed	% of particles having wt. % mineral matter as							
		0-5	5-10	10-25	25-40	40-55	55-70	70-85	85-100
+90	282	91	3	1	-	-	-	-	-
-90+75	351	89	3	1	-	-	-	-	-
-75+60	558	89	3	1	1	1	-	-	-
-60+45	704	88	5	1	1	1	1	1	1
-45+30	698	88	4	1	1	1	-	2	3
-30+20	718	88	3	1	1	1	2	2	2
-20+8	822	86	2	1	1	1	2	3	4
TOTAL	4,261	87	5	1	1	1	1	2	2

Table 10

Distribution of Estimated Total Mineral Matter in Rosebud Coal

Size fraction μm	number of particles analyzed	% of particles having mineral matter as:							
		0-5	5-10	10-25	25-40	40-55	55-70	70-85	85-100
+90	278	88	6	2	1	1	1	1	-
-90+75	373	83	10	3	1	1	1	2	-
-75+60	522	83	7	2	1	1	2	2	1
-60+45	530	82	7	2	1	1	2	2	2
-45+30	659	82	6	2	1	1	3	2	2
-30+20	598	75	5	2	2	1	4	4	6
-20+8	899	72	5	2	2	1	5	5	7
TOTAL	3,849	78	6	2	2	2	3	3	4

Results and discussion

The data on the two coals is presented in Tables 11 and 12. Studies by Raask⁽¹⁶⁾ indicated that agglomeration of fly ash particles in the hot flue gas stream was a rare occurrence. However, the studies of Ramsden⁽¹⁷⁾ indicated that the molten inclusion of ash formed during the combustion of a coal particle might or might not be dispersed in the gas stream as minute droplets. This dispersal was believed to occur if the carbon framework disintegrated during combustion. This disintegration was expected to be influenced by the petrography of a particle; hydrogen rich waxy materials like exinites, resinites, alignites and scleronites might well disintegrate. Shibaoka⁽¹⁸⁾ performed hot stage microscopy studies on vitrite particles (containing vitrinite greater than 95%) and found that these expanded rapidly and then shrank without disintegrating. Fusinite particles, containing fusinite macerals greater than 95%, were found in the same study to expand very slightly and not explode. The petrographic analysis of the two coals (Table 5) indicates that these coals have only small proportions of exinite material and hence most of the particles are not expected to explode. Shibaoka also found that vitrite particles leave behind very fine ash particles. But this would not be expected if the coal particle has an ash composition such that the ash would melt. Such ash particles would be mobile on the carbon surface in view of the non-wetting characteristics of slag on a carbonaceous surface⁽¹⁹⁾, with agglomeration leading to a droplet of ash.

Recently Padia⁽²⁰⁾ has claimed that about 5 ash particles per coal particle are formed on combustion of bituminous coal. His analysis implied that the distribution of mineral matter was uniform in the coal particles, independent of particle size, which the present study indicates is not valid. Table 10 shows that 25% of particles by weight have mineral matter varying from 5 to 100%. In the absence of definitive experiments, it is assumed that one coal particle produces one ash particle or that if more than one ash particle is formed from one coal particle, the composition of each satellite ash particle is the same.

From Tables 11 and 12 one can see a major difference between the two coals in terms of the fraction of ash occurring as Type IV compositions; Comanche has 7.5% of the ash in Type IV, Rosebud 47%. Since 1550°C approximates a typical flame temperature in a pulverized coal fired boiler, the ash of Type IV particles would be molten and sticky in the boiler environment. Such particles would hence have a better chance of adhering to the heat transfer surfaces, leading to initiation of deposit formation.

In addition, some particles of Type II and Type III would also lead to sticky particles. It was difficult to compute the liquidus state of such particles because of the lack of complete data on liquidus temperature for the systems $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ or $\text{CaO-FeS}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$. However some general conclusions can be drawn based on the information available in literature⁽²¹⁾ on the systems $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO}$ and $\text{Fe}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$. It seems that compositions containing Fe_2O_3 in excess of 50% would have

Table 11

Wt.% Distribution of Different Particle Types
in Various Size Fractions of Comanche Coal

Coal Size fraction μm	Type I	Type II					Type III					Type IV	Type V
		wt.% of FeS ₂ in ash composition					wt.% of Fe ₂ O ₃ in ash composition						
		0-5	5-10	10-25	25-50	50-100	0-5	5-10	10-25	25-50	50-100		
+90	0	6	3	1	-	-	6	1	1	-	-	22	60
-90+75	1	5	4	1	1	-	5	3	-	-	-	17	63
-75+60	4	6	5	2	1	1	6	4	2	-	-	16	53
-60+45	4	4	5	3	1	-	8	5	4	-	1	14	51
-45+30	4	4	3	6	1	-	4	6	4	-	-	12	56
-30+20	6	2	3	6	1	-	3	5	8	2	1	10	53
-20+8	6	2	1	5	1	1	2	4	5	2	1	14	56
Wt.% of coal particles containing each Type													
TOTALS	4.3	3.7	3.1	4.1	1.0	0.5	4.3	4.5	3.8	0.8	0.5	14	55.7
Wt.% of total mineral content of each Type													
TOTALS	0.3	2.8	3.4	1.9	1.6	1.9	7.5	6.8	2.2	2.7	2.4	7.5	59.0

Table 12

Wt.% Distribution of Different Types of Particles
in Various Size Ranges of Rosebud Coal

Size fraction μm	Type I	Type II wt.% of FeS_2 in ash composition					Type III wt.% of Fe_2O_3 in ash composition					Type IV	Type V
		0-5	5-10	10-25	25-50	50-100	0-5	5-10	10-25	25-50	50-100		
+90	4	4	1	2	2	-	1	2	2	1	-	49	32
-90+75	4	1	2	2	1	-	1	1	2	2	-	52	32
-75+60	6	1	1	1	2	-	1	1	2	-	-	49	36
-60+45	7	2	2	2	1	1	1	3	3	1	1	42	34
-45+30	6	2	2	2	1	1	2	3	4	3	1	35	38
-30+20	10	1	3	2	1	1	1	2	4	3	2	39	31
-20+8	14	2	3	6	2	2	2	3	6	2	3	27	28
Wt.% of coal particles containing each Type													
TOTALS	8.9	1.7	2.5	3.4	1.5	1.0	1.5	2.4	4.0	1.6	1.5	38.0	32.0
Wt.% of total mineral content of each Type													
TOTALS	0.6	2.1	1.8	1.1	1.2	1.2	7.8	2.9	6.8	3.8	3.5	47.0	25.2

liquidus temperatures as low as 1550°C. Compositions containing less than 50% Fe₂O₃ may also be sticky, but that would depend on the amount of the rest of the constituents. Information on systems containing FeS₂ or FeS is minimal, but in view of the low liquidus temperature of FeS₂ (less than 1200°C) it is expected to flux more effectively most of the compositions, if it is not converted to iron oxide. The studies by Moza et al⁽²²⁾ indicate that when FeS₂ is melted in an oxidizing atmosphere in a few seconds, it produces mostly FeS. FeS is not expected to behave differently from FeS₂ in terms of its fluxing action because FeS also has a low liquidus temperature (less than 1200°C).

It is concluded that particles containing ash with more than 50% of Fe₂O₃ would most likely be sticky in a boiler and particles containing 25% or above of FeS₂ might also be sticky. If in addition to Type IV particles, particles containing ash with FeS₂ greater than 25% and Fe₂O₃ greater than 50% are included among the possibly sticky particles, Rosebud coal would have 51.7% of the ash in such particles in comparison to 11.8% in Comanche coal.

It is clear that to characterize the slag deposit properties of pulverized coal using the SEM analysis technique described here, it will be necessary to have a much more detailed understanding of the mechanism of slag deposit formation. The data output of the technique can be readily manipulated by the computer to calculate the amounts of different types of particle, if only the characteristics of bad acting particles were established to define the types of importance. It is, of course, also possible that the technique described here might have application in other areas of coal investigation.

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2.5.5. NOTE: A NEW TEST FOR CHARACTERIZING THE SLAG
DEPOSITION PROPERTIES OF A COAL ASH:
THE STICKING TEMPERATURE

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Summary

When coal ash melts in a p.c. flame it forms a droplet of molten glass, which can adhere to the metal tubes in the upper regions of a boiler furnace. A laboratory test has been developed to study the adhesion process. A small pellet of ash molded on a platinum wire is melted in a gas flame and the droplet of slag falls off the wire. It falls a short distance onto a metal substrate held at a controlled temperature. We have found that if the substrate is below a critical temperature, the "sticking temperature," it will not adhere. Addition of FeO to a coal ash reduces the sticking temperature on steel from nearly 500°C to under 400°C .

One of the problems caused by slagging of mineral matter contained in coal is that of fly ash sticking in the upper regions of a water tube boiler furnace where the temperature is not high enough to cause the slag to become fluid, and large masses of fused slag can build up.⁽¹⁾ When these break off under their own weight, the falling mass can severely damage tubes at the bottom of the furnace.

During investigations of various facets of this problem under a DOE research contract, we have discovered that a liquid slag droplet falling onto a metal surface sticks to the surface if the metal temperature is above a critical temperature and does not stick if it is below this temperature. We will call this temperature the *sticking temperature*. If the sticking temperature is T_s for a particular composition of slag droplet, this means that the droplet can stick to the surface of the water tubes all the way from the bottom of the furnace where $T > T_s$, up to where the surface temperature of the metal reaches T_s . If T_s is low, the region of adherence will extend into the upper parts of the furnace.

The tests were performed as follows. A small pellet of coal ash, or synthetic mixture of powdered mineral matter, was prepared by mixing the powdered material with 15% water and 0.5% binder (polyvinyl alcohol) and hand tamping the material into a hole of 3mm diameter x 6mm deep in a metal die into which a loop of platinum wire was inserted. The die was inserted into a furnace at 150°C for 6 hours, after which the platinum wire could be lifted out with the pellet of test material sintered around the platinum loop at the end. This was lowered into a vertical refractory tube. A flame of oxygen-methane was directed at the pellet through a hole

in the wall of the tube causing rapid fusion and melting. The molten slag droplet falls off the wire onto a substrate situated just below the bottom of the tube furnace. This substrate consisted of a stainless steel rod of 15mm diameter and 100mm long. It was enclosed in a quartz tube which was electrically heated by resisting wires wound round it. There was a small block of mild steel resting on the top of the stainless steel rod. This metal block contained a hole drilled to receive a Pt-Rh thermocouple. By varying the power to the heating coils of the substrate the metal temperature was varied from 30°C to 750°C. The length of fall from the platinum loop to the metal was 30mm, and calculations show that the droplet does not lose much heat during the fall. Thus the test simulates a droplet of slag leaving a hot flame and rapidly striking a cooled substrate such as a boiler water tube.

The droplet solidifies on contact with the metal. If the metal is above T_s the droplet adheres so that the droplet cannot be blown off the surface. If the metal is below T_s , the droplet does not adhere and the droplet is readily blown off of the surface, or rolled off by tipping the substrate. Even with this crude apparatus the value of T_s can be determined within a range of $\pm 10^\circ\text{C}$.

The physical process occurring in the adhesion or non-adhesion of the droplet can be tentatively described as follows. The droplet is still molten when it strikes the metal, but the contact with the metal causes an immediate cooling and solidification. The surface tension of slag-metal-air creates an adhesion and there may be chemical reaction, but the solidification causes stress due to contraction or expansion of the material bonded

to the surface. When the metal temperature is above T_g , the adhesion force is strong enough to allow a continuing bond to the surface after solidification has occurred. When the metal temperature is below T_g , the solidification is rapid enough to crack away the slag from the metal. The parameters of importance are presumably surface tension, viscosity (plasticity), thermal conductivity and coefficient of expansion, surface roughness and surface composition.

It was demonstrated that T_g is sensitive to the composition of the slag droplet. A coal ash was doped with different amounts of FeO and the adhesion temperature noted. Figure 1 shows T_g versus the content of FeO in the ash. There is a definite decrease in the sticking temperature as the FeO content is increased. The curve starts at 1.78 weight % FeO which is the original FeO in the coal ash. This coal ash had about 50% mixed layer clays, 28% quartz, and the rest of various minerals.

This investigation is continuing, with variables to be studied including size of pellet, surface tension, shear force to dislodge the solidified droplet, mineral composition, oxidizing or reducing gas conditions, metal, surface treatment of metal, deposited films of alkali on metal, etc.

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Figure 1. Values of sticking temperature plotted against content of FeO in the ash.

2.5.6. The Sticking Temperature and Adhesion Force of Slag
 Drops from Four Coals on Mild Steel

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INTRODUCTION

Moza and Austin⁽¹⁾ have recently introduced the concept of the sticking temperature T_s of a coal ash as a useful index of slag deposit formation in the upper part of a utility boiler furnace. They report that a molten droplet of coal ash falling onto a cooled metal substrate will stick if the substrate temperature is higher than T_s and will not stick if it is lower. A low sticking temperature means that slag deposits may form higher in the furnace in addition to the hot regions near the flame. Once a deposit is initiated in the cooler upper regions addition of further ash can create a hanging mass which can fall and damage the bottom tubes. In this paper we will expand this concept to make it more quantitative by considering the strength of adhesion of the droplet to the substrate. Results are reported for four coal ashes from coals used in utility boilers.

EXPERIMENTAL APPARATUS

The apparatus used for the tests is shown in Figure 1. A pellet of ash formed on the end of a platinum wire is suspended from a 316 stainless steel support rod which is threaded through a stainless steel cap. Screwing the rod up or down enables the pellet to be accurately located in a 25mm long vertical alumina tube of 10mm internal diameter and 1mm wall thickness, which contains a Pt-Rh thermocouple. This tube is cemented into a vertical alundum tube which is 85mm long by 25mm internal diameter with a wall thickness of 2.5mm. This outer furnace tube has two 15mm diameter holes located opposite the internal tube, so that two flames can be used to heat the inner furnace tube. This arrangement is mounted on a stainless steel cap which is in turn bolted to the transite top of an electric heating furnace used to control the temperature of the test substrate.

The bottom heating furnace consists of a cylindrical stainless steel shell 100mm high and 20mm diameter with top and bottom of transite discs 10mm

thick. The heating element is wound round a centrally located alumina tube of 25mm internal diameter and 3mm thick which contains a stainless steel cylinder to conduct heat to the test substrate. This cylinder has a stainless steel cylinder top of 45mm diameter containing a cut-out of 25mm diameter by 5mm deep to contain a disc of the substrate. The steel cap connecting the melting furnace with the substrate furnace has a central top hole which allows the molten droplet falling off the platinum wire to strike the substrate after a fall of 30mm. The cap also contains holes in the side to allow the droplet-substrate contact to be viewed, to pass a thermocouple wire to a 2mm diameter hole drilled in the substrate, and to admit gas to control the atmosphere around the substrate and pellet if necessary. The substrate furnace has a 50V, 10 amp variable power supply so that the temperature of the substrate can be varied from room temperature to 750°C.

The connected furnaces are mounted on a hinge at the base which is in turn attached to a steel base plate with leveling screws. The hinge enables the system to be tipped so that the horizontal substrate with the attached frozen slag droplet is put into a vertical position. A hole in the side of the stainless steel cap is then directly under the droplet-substrate interface, which enables a stainless steel rod to be pushed against the droplet.

Figure 2 shows the mounting of the ram to replace the pan of a top loading balance, with the balance resting on the platform of an hydraulic jack (12 ton capacity supplied by Walker Manufacturing Co. of Racine, Wisconsin). The ram is 14mm diameter at the base with a 60mm long tip of 3mm diameter, and the ram is raised 1mm by one complete stroke of the jack handle. The droplet on the substrate is viewed with a cathetometer X-Z measuring machine (Titan Tool Supply Co., Buffalo, N.Y.) with a 200mm focal length microscope and horizontal and vertical displacement measurement over a range of 2.50mm with a least count of 0.025mm.

EXPERIMENTAL METHODS

Pellets of ash are made in 4mm diameter holes drilled in an aluminum plate of 4mm thickness, giving a pellet weight of 120-150mg. About 5 grams of ash (ashed according to the ASTM standard ash test) are mixed with 0.5ml of water and two drops of 10% polyvinyl alcohol solution to act as binder. The aluminum mold is sprayed with mold releasing agent (supplied by Miller Stephenson Chemical Co., Danbury, Conn.) and the twenty holes in the mold filled with the ash paste. A suitable length of 0.3mm diameter Pt wire is inserted in each pellet and the filled mold dried in an oven at 120°C for 1 hour. After cooling, the pellets are gently removed from the mold. A pellet is mounted in the test furnace to coincide with the bottom of the inner furnace tube.

The upper furnace is heated by oxygen rich oxygen-methane flames (1750-1850°C) until the pellet melts and falls onto the substrate. The droplet solidifies immediately on contact. The height and base of the droplet are measured to estimate the contact angle. The arrangement is tipped, with the substrate furnace still at the controlled temperature. If the droplet does not fall off, the ram of the adhesion tester is gently raised to contact the droplet. The jack is raised slowly and the reading of the balance when the solid droplet shears off is taken as the adhesion force. This measurement can be made with an accuracy of about 0.3 grams.

The sticking temperature is defined as the temperature at which the droplet just sticks when the apparatus is tipped to the vertical position. Below this temperature the droplet will fall off on tipping. Since the substrate temperature was varied in 10°C steps, the sticking temperature can only be quoted to the nearest 10°C interval. At least four tests were run to determine this temperature for each ash.

RESULTS

The thermocouple in the melting furnace indicated that the droplets fall off the wire at 75 to 150°C above the initial ash melting point. It takes about 15-20 seconds for melting and fall and a heat transfer estimation suggests that the loss of temperature of the droplet as it falls is no more than about 70°C before it touches the substrate. In the tests reported here the substrate was a polished (No. 400 grit) mild steel disc which was preconditioned at 500°C for 50 hours in air to develop an oxide film. The four coal ashes tested are shown in Table 1.

For these ashes on the mild steel substrate it was found that the reproducibility of the adhesion force was within about $\pm 4\%$ when the force was beyond 10 grams and $\pm 10\%$ when the force was below 5 grams. The temperature of the substrate during melting, adhesion and strength testing was constant within $\pm 5^\circ\text{C}$. The contact area between the solidified droplet and the substrate ranged from 0.08 to 0.13cm^2 .

Figure 3 shows the force versus substrate temperature results. At the higher temperature, e.g. 600°C , the adhesion strength was approximately 5000gcm^{-2} for Upper Freeport coal, 500gcm^{-2} for Texas lignite, 150gcm^{-2} for Wyoming coal and 50gcm^{-2} for Illinois Coal. Extrapolating the results to zero sticking force gave the sticking temperatures as 460°C , 430°C , 475°C and 500°C for the four coals in the same order. The direct measurements gave values of 460°C , 430°C , 470°C and 500°C , respectively. Thus from the point of view of sticking temperature the worst coal is Texas lignite. On the other hand, Upper Freeport coal gives the highest adhesion strength at temperatures above 500°C .

Figure 4 shows the variation of the contact angle α between the solidified droplet and the substrate for the Upper Freeport coal, where the contact angle is calculated from

$$\tan(\alpha/2) = 2h/b \quad (1)$$

h is the height of the drop and b the diameter of the contact area. The correlation between this contact angle and the adhesion force shows that the droplet spreads more on the surface as the sticking temperature is exceeded.

CONCLUSIONS

Although it is clear that much work remains to be done to characterize the sticking properties of droplets of coal ash on various substrates, the above results show that a valid comparative technique has been developed. The sticking behaviour of the droplets formed from coal ash is quite different from one coal to another. The sticking temperatures ranged from 430°C to 500°C, and the differences in adhesion force were even more pronounced.

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FIGURE CAPTIONS

- Figure 1. Illustration of melting furnace mounted on substrate furnace.
- Figure 2. Arrangement for measuring the adhesion force.
- Figure 3. Slag droplet adhesion force as a function of substrate temperature for four coal ashes and oxidized mild steel.
- Figure 4. Variation of contact angle with substrate temperature for ash from Upper Freeport coal.

Table 1: Analysis of Coal Ashes

Ash wt.% constituent	Pennsylvania, HV. Upper Freeport, Bituminous	Illinois No. 6 Bituminous	Wyoming sub-bituminous School	Texas Lignite Wilcox
% ash in coal	17.1	12.3	19.9	15.0
SiO ₂	52.36	49.7	50.9	47.7
Al ₂ O ₃	27.88	15.8	19.0	12.0
TiO ₂	1.87	1.3	1.3	2.1
Fe ₂ O ₃	9.5	13.0	7.7	4.7
MgO	1.0	0.9	2.2	2.9
CaO	1.96	6.5	11.8	15.0
Na ₂ O	0.39	1.1	0.3	0.6
K ₂ O	3.34	1.9	1.3	0.4
SO ₃	1.70	7.0	5.5	14.6

FIG. 1 Illustration of melting furnace mounted on substrate furnace

FIG. 2 Arrangement for measuring the adhesion force

FIG. 3 Slag droplet adhesion force as a function of substrate temperature for four coal ashes and oxidized mild steel

FIG. 4 Variation of contact angle with substrate temperature for ash from Upper Freeport coal

STUDIES ON SLAG DEPOSIT FORMATION IN PULVERIZED COAL COMBUSTORS

PART I: RESULTS ON THE WETTING AND ADHERENCE OF SYNTHETIC
COAL ASH DROPS ON STEELS

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Introduction

When a pulverized coal particle is burned the mineral matter associated with the particle melts to form drops of molten glass. The large water tube boilers used for steam raising for power generation are commonly fired with pulverized coal. Adherence of the glassy drops can form slag coatings in the hotter parts of the boiler furnace. Of particular concern is adherence in the upper region of the furnace at the screen tubes, since the accumulation of a large mass of fused slag which then breaks away and falls can seriously damage the bottom tubes. As part of a project concerned with various aspects of this problem, a laboratory test has been developed^(1,2) which is an indication of the ability of a molten drop to adhere to a cooler substrate.

It was demonstrated⁽²⁾ that the test gave different behavior for different coals, but the reasons for the differences in behavior were not elucidated. This paper is a report on results obtained with this test using mixtures of pure metal oxides of the type that occur in coal ash, with compositions designed to increase an understanding of the basis of the sticking mechanism.

Experimental Techniques

The apparatus described previously⁽²⁾ has been modified to give easier operation. The test consists of forming a small pellet (about 0.1g) from a mixture of synthetic ash on the end of a platinum wire. The pellet is positioned at the center of two opposed methane-oxygen flames so as to heat the pellet to temperatures up to 1700°C. After melting, the viscosity decreases until the molten drop falls off. It falls about 40-50 mm through a hole on to a horizontal substrate maintained at a controlled temperature by an auxiliary electric heater. The drop freezes on the substrate and adheres or does not adhere, depending on the composition of the drop, and the temperature and material of the substrate. If it adheres, the drop is sheared off the substrate (still at the controlled temperature) by a ram moving parallel to the surface, and the shearing force required is measured. An apparent contact angle α is calculated from the equation

$$\tan (\alpha/2) = 2h/b \quad (1)$$

where h is the height of the drop and b is the diameter of the contact area.

In the tests discussed here, the metal substrates were washed in acetone, wet polished to smoothness with 400 grit Caribimet paper, washed with distilled water, dried with tissue paper and oxidized in air in a furnace at 400°C for 20 hours. Most of the tests were performed using a synthetic coal ash mixture containing 37 weight % CaO, 20.4 SiO₂%, 18.9 Al₂O₃ and 23.7% Fe₂O₃, ground together with a mortar and pestle. This mixture was chosen because it could be easily melted (liquidus temperature 1480°C) and its viscosity is low enough that the drop falls from the wire at around 1650-1700°C. Tests

were also conducted with pure mineral pyrite. The substrates tested were a low carbon, low manganese mild steel ($C = 0.2\%$ and $Mn = 0.5\%$), a high carbon, high manganese mild steel ($C = 0.44\%$ and $Mn = 0.8\%$) and two stainless steels (SS304 and SS316).

Results and Discussion

Pellets of the synthetic ash mixture of CaO , Al_2O_3 , SiO_2 and Fe_2O_3 were melted and dropped onto an oxidized mild steel substrate held at a temperature of $480^\circ C$. At this temperature the molten drop stuck to the substrate upon solidification. High speed photography at 1000 frames per second gave the following picture of solidification and adherence under these conditions (see Figure 1). The drop was molten when it struck the surface and it flattened somewhat on impact, then reverted within 3 milliseconds to a shape nearer that of a sphere, flattened somewhat again, etc. The contact area solidified almost instantaneously and a zone of solidification moved up through the drop, giving complete solidification in 30 to 40 milliseconds. The rate of chilling of the interface was, therefore, roughly $10,000^\circ C \text{ sec}^{-1}$, so that it was unlikely that chemical or phase equilibrium was reached at the interface. It was also expected that the interface would be a glass with little crystallinity (see discussion below).

Pellets of the synthetic mixture were heated up to $1400^\circ C$ (below the liquidus temperature) in a platinum crucible and tipped onto a mild steel substrate whose temperature was varied from $25^\circ C$ to $700^\circ C$. There was no adherence. These experiments indicated that melting of the ash was necessary for sticking.

Next, pellets of the synthetic ash mixture were melted, dropped in air to cool and collected. The cooled drops were held by platinum wires attached to steel forceps, and heated for different times in the methane flame before being dropped on to stainless steel coated with a 2mm thick layer of sodium hydroxide. The substrate temperature was kept constant for a set of experiments, and for each experiment the substrate was tilted to find if the drop was sticking or not. A thermocouple positioned near the surface of a pellet was used to construct a calibration curve between the time of heating of the pellet and its temperature, for constant flame conditions. From the calibration curve, it was then possible to find the initial drop temperature at which sticking would just occur for a given substrate temperature. The results are shown in Figure 2. Sticking always occurred if the substrate temperature was above $293^\circ C$, which corresponded to the temperature at which the NaOH substrate showed the first signs of melting. This temperature is somewhat lower than the melting point of NaOH ($318^\circ C$), possibly due to impurities dissolved from the substrate metal into the NaOH coating. Sticking was observed at even lower substrate temperatures as long as the initial drop temperature was higher than $340^\circ C$. It was observed visually in these experiments that when sticking had occurred, some or all of the contact area with the substrate was melted, so it was

concluded that for sticking to occur either the substrate should be molten or the temperature of the drop should be such that it can cause melting at the point of contact with the substrate.

Figure 3 shows the force of adherence and the apparent contact angle for the drop formed from the synthetic mixture falling onto an oxidized low carbon mild steel substrate. Adhesion was sufficient to prevent the solidified drop from falling off the substrate when it was tipped vertically when the temperature was about 460°C, which was defined as the sticking temperature (T_s). Over the relatively small range of substrate temperature shown in the figure the adhesion strength σ based on a contact area of 0.28 cm² was given approximately by

$$\sigma = \exp[(T - T_s + 0.5)/2] \text{ g/cm}^2 \quad (2)$$

where T is the substrate temperature in °C. Thus the strength of adhesion increased exponentially as the substrate temperature was increased above the sticking temperature. The degree of wetting of the surface achieved in the few milliseconds of freezing is shown by the apparent contact angle. The contact angle decreased and wetting increased as the substrate temperature increased.

After the drop was sheared off, it was polished in a vertical plane and viewed in a scanning electron microscope. Figure 4 shows the results; the dark area on the left is the epoxy mounting medium. The region in the drop next to the substrate/drop interface was clear glass, and crystallinity developed about 500µm away from the interface, see Figure 4a. The irregular dark areas in the crystallized area on the right correspond to crystallization of an iron-deficient phase. The rounded dark areas are bubbles in the glass. At higher magnification, Figure 4b, a layer of iron oxide sticking to the drop at the interface was clearly visible. This layer had been broken off the substrate, but it did not appear to adhere smoothly and perfectly to the glass, or to cover the whole surface. It was approximately 8µm in thickness.

Using an electron microprobe, characteristic x-rays were collected at points along a line passing from the iron oxide layer to the glass. The x-ray intensities were normalized and plotted as a function of the distance from the interfacial region between the oxide layer and the drop. The results are shown in Figure 5, where the negative distance corresponds to the oxide layer region. Using the Kanaya and Okayama⁽³⁾ equation, the x-ray emission volume for iron oxide and the glass are expected to be about 2.5µm and 3.3µm in diameter respectively at the acceleration voltage used. From these emission volume figures, it appears that there was an inter-diffused interfacial region of some small but finite thickness between the drop and the iron oxide layer.

Figure 6 shows the results of perpendicular viewing of the interface, for substrate temperatures of 400, 450 and 500°C. The white patches were shown to be iron oxide. The smooth patches are areas where the glass apparently did not wet the metal, since they did not show the polishing striations of the substrate. Some holes caused by bubbles were also

present. It was concluded that the adhesion strength was due to a very rapid interaction of the glass with the oxide layer on the mild steel, but that this interaction was stronger at certain patches and was not uniform over the whole surface. When the drop was sheared off, the strongly reacted patches of oxide film broke off the metal, while glass broke off the oxide at the weak areas. As the substrate temperature increased, the patches of strong interaction were more numerous and larger in area. At 500°C the patches represented about 25% of the contact area and with a shearing force of 89 g, this represented a shear strength of the oxide film of about 3000 g/cm².

Figure 7 shows the SEM results of perpendicular viewing of that area of the substrate where the drop has struck the surface. During this particular experiment, the substrate temperature was 500°C. Figure 7a, a secondary electron image of the substrate, shows that patches of oxide were peeled off the metal, exposing bare metal. Figure 7b shows a back-scattered electron image of a different portion of the substrate. The white patch at the edge corresponds to bare metal. It appears that patches as big as 400µm in diameter had been peeled off.

Substrates of two stainless steel (SS304 and SS316) were polished and heat-treated in air at 400°C as described previously. The results of sticking tests with the synthetic mixture are included in Figure 3. The drop showed poor wetting of the stainless steel surface and a low adhesion force up to substrate temperatures of 590°C. Stainless steels also showed lack of any chemical interaction with the drop up to temperatures of 530°C.

Substrates of mild steel were coated with 10% NaCl-H₂O solution, covered with a glass slide to squeeze out the liquid, and the resulting sandwich was freeze-dried. After removal of the slide, the increase in weight corresponded to a layer of NaCl on the metal of about 50µm thick. The procedure was repeated for SS304. Sticking tests on these substrates gave the results shown in Figure 8. On mild steel the drops stuck at all substrate temperatures and developed a shear strength at 400°C comparable to that on uncoated mild steel at 500°C. Drops also adhered on the coated stainless steel substrate, giving the same strength of adhesion as on uncoated mild steel at 525°C. It was concluded that the NaCl melted when the drop struck and fluxed the glass, to give increased adhesion. Figure 9 shows a perpendicular SEM view of the drop. It appeared that NaCl was completely melted and assimilated by the drop. Figure 10 shows the perpendicular view of the substrate; 10(a) shows the patches of iron oxide layer removed from the substrate. This same substrate was polished to remove as much of the oxide as possible without removing too much of the metal and it was again observed under a scanning electron microscope, see Figure 10b. This revealed some dark spots showing that iron oxide still existed in some places. Further polishing of the substrate suggested that these spots were fairly deep. The same spots were not observed on the uncoated oxidized mild steel substrate.

The synthetic mixture was modified by the addition of 12% weight of FeS_2 . The result is shown in Figure 11. The presence of pyrite in the droplet caused the sticking temperature to fall to about 200°C , and increased wetting of the mild steel surface. A given adhesion strength was reached at about 70°C lower temperature than for the synthetic mixture. The droplet was further analyzed chemically and found to contain about 3% sulfur, indicating that during melting the sulfur did not burn off completely. The phase relations for this system indicate⁽⁴⁾ that the liquidus temperature is lowered by the addition of more iron.

The synthetic mixture was modified by the addition of 10% weight of NaCl . The result is shown in Figure 12. The presence of NaCl in the pellet decreased the sticking temperature to about 110°C , with improved wetting of the surface. A given adhesion strength was reached at about 200°C lower temperature than for the synthetic mixture alone. Chemical analysis of the drop indicated that it had 1.22% weight Na and 1.36% Cl, showing that much of the NaCl was lost during melting. The sodium content was somewhat in excess of stoichiometric proportions in NaCl suggesting that some sodium had preferentially combined with other ingredients of the pellet. It is to be expected that sodium would reduce the liquidus temperature of the drop.

High purity pyrite (FeS_2) supplied by the Smithsonian Institute, Washington, D.C., was used for making pellets. The pellets were melted and dropped onto an oxidized mild steel substrate. The results are shown in Figure 13. The pyrite drops showed excellent wetting of the substrate, the contact angle at the sticking temperature being 76° . These drops also showed high sticking strengths. X-ray diffraction studies on these drops indicated that they contained predominantly pyrrhotite $\text{Fe}(0.995)\text{S}$; small amounts of magnetite, and no wustite, pyrite or hematite. The chemical analysis of a drop confirmed it contained approximately 86.6% pyrrhotite and 13.4% of Fe_3O_4 . In these experiments, the time taken to melt the pyrite was 10-15 seconds, which is much longer than the time the pyrite particle would remain in the flame region in a boiler, although the drop was of course much larger than a fly ash particle. It is possible that during combustion in a boiler pyrite particles might stick to metal surfaces as pyrrhotite and then subsequently become oxidized to iron oxides.

Figure 14 shows an SEM perpendicular view of the drop formed from pyrite. The bright patches are iron oxide, the darker ones probably are pyrrhotite and the darkest (indicated by arrow) were found to have higher percentages of sulfur in them than the rest. It was not possible to decide whether the bright particles of iron oxide came from the substrate or the drop or both. Figure 15 shows the perpendicular view of the substrate. Figure 15a indicates that patches of oxide layer were peeled off the substrate, exposing bare metal shown as the white area in Figure 15b. Figure 15c shows an enlarged view of the spotty region of substrate in Figure 15b. The dark lines indicate sulfur-rich areas. Possibly sulfur has accumulated along grain boundaries in the oxide layer. The substrate was then polished repeatedly to expose

as much of the bare metal as possible. Figure 15d, shows a back-scatter image of this polished metal substrate. The dark area was found to contain more sulfur than the rest of the metal, indicating that either the sulfur from the drop has diffused into this area or the pyrite drop had penetrated to this area by flow into cracks in the oxide film.

Conclusions

For an ash drop to stick strongly to a colder metal surface it is necessary that the interfacial region between the two should be liquid in its initial stages of formation.

There is a distinct temperature of the substrate above which ash drops will stick to it and below which they will not stick. This was defined as the sticking temperature (T_s). The strength of adherence increases approximately exponentially as the temperature of the substrate is increased.

The oxide layer on a mild steel substrate plays a crucial role in the sticking of ash drops. It appears that ash drops adhere to the oxide layer and upon shear parts of this oxide layer are broken off the substrate. This indicates that adherence between the oxide layer and ash drop is stronger than the adherence of oxide layer to the metal.

Ash drops show poor sticking on stainless steel substrates when compared to oxidized mild steels, probably because of the lack of thick oxide layers on stainless steel.

The interaction between the molten ash drop and colder oxidized metal surface seems to be of a chemical nature. This interaction takes place in a very short time, probably in milliseconds, and extends over a region of a few micrometers.

The sticking of the ash drop is greatly enhanced when the metal surface is coated with sodium chloride, probably because sodium chloride can flux the interface of the ash drop at the surface.

The sticking is also enhanced by the presence of NaCl or FeS₂ in the drop itself. Sodium, chlorine and iron are expected to lower the liquidus temperature of the composition used. However, most but not all of the sodium chloride or sulfur is driven out of the drop during melting. In the case of sodium chloride, it seems that some of the sodium is able to react within the ash drops during melting.

Pyrite drops adhere very strongly to the oxidized metal substrates and the results indicate some pitting or penetration of the metal. Further, pyrite drops stick to substrates in the form (predominantly) of pyrrhotite (Fe_{0.995}S) drops.

Future papers will explore the effect of treatments of the substrate surface and drop composition, and the correspondence of these test results to adherence in a small scale pulverized coal fired furnace.

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Figure Captions

- Figure 1. Collision of drop with oxidized mild steel substrate held at 480°C (above sticking temperature): frames at 1000 per second from top left hand corner down.
- Figure 2. Sticking region temperature as a function of temperature of drop and of substrate (NaOH on stainless steel).
- Figure 3. Slag drop adhesion force and contact angle as a function of substrate temperature for three different substrates.
- Figure 4. Electron back-scatter image of a vertical section of glass drop at substrate interface at different magnifications.
- Figure 5. X-ray profiles of various elements as a function of distance from the interface, substrate at left (acceleration voltage: 15kV).
- Figure 6. Secondary electron image of perpendicular view of the drop interface for substrate temperatures a) 400°C; b) 450°C and c) 500°C.
- Figure 7. a) Secondary electron image of perpendicular view of the substrate where drop had struck:
b) Electron back-scatter image of perpendicular view of the substrate (at a different plate).
- Figure 8. Slag drop adhesion and contact angle as a function of substrate temperature, for substrates coated with sodium chloride. Curve for oxidized mild steel is shown for comparison.
- Figure 9. Secondary electron image of perpendicular view of the drop interface for NaCl-coated substrate: substrate temperature 500°C.
- Figure 10. a) Secondary electron image of the sodium chloride-coated substrate, in drop collision region
b) Back-scatter image of the polished substrate of the same area as in Figure 10a.
- Figure 11. Effect of pyrite addition to pellet on adhesion force and contact angle, oxidized mild steel substrate.
- Figure 12. Effect of NaCl addition to the pellet on adhesion force and contact angle.
- Figure 13. Pyrite drop adhesion force and contact angle as a function of substrate temperature.
- Figure 14. Electron back-scatter image of perpendicular view of the drop interface, pyrite on oxidized mild steel: substrate temperature 500°C.

- Figure 15.
- a) Secondary Electron Image of the substrate
 - b) Back-scatter image of the substrate of the same area as in (a)
 - c) Back-scatter image of the dark spotty region of the substrate as shown in (a) or (b).
 - d) Back-scatter image of the polished substrate of the same area as in (a) or (b).

Figure 1: Collision of drop with oxidized mild steel substrate held at 480°C (above sticking temperature): frames at 1000 per second from top left hand corner down.

Figure 2: Sticking region temperature as a function of temperature of drop and of substrate (NaOH on stainless steel).

Figure 3: Slag drop adhesion force and contact angle as a function of substrate temperature for three different substrates.

Figure 4: Electron back-scatter image of a vertical section of glass drop at substrate interface at different magnifications.

Figure 5: X-ray profiles of various elements as a function of distance from the interface, substrate at left (acceleration voltage: 15kV).

Figure 6: Secondary electron image of perpendicular view of the drop interface for substrate temperatures

a) 400°C, b) 450°C and c) 500°C

(a)

(b)

Figure 7: a) Secondary electron image of perpendicular view of the substrate where drop had struck:
b) Electron back-scatter image of perpendicular view of the substrate (at a different plate).

Detachment F. Contact A.

—●—

—○—

MILD STEEL

—▲—

—△—

NaCl COATED SS 304

—■—

—□—

NaCl COATED MILD STEEL

Figure 8: Slag drop adhesion force and contact angle as a function of substrate temperature, for substrates coated with sodium chloride. Curve for oxidized mild steel is shown for comparison.

Figure 9: Secondary electron image of perpendicular view of the drop interface for NaCl-coated substrate: substrate temperature 500°C.

(a)

(b)

Figure 10: a) Secondary electron image of the sodium chloride-coated substrate, in drop collision region
b) Back-scatter image of the polished substrate of the same area as in Fig. 10(a).

Detachment F. Contact A.

—○—

—○—

NO PYRITE IN SAMPLE

—■—

—■—

12% PYRITE IN SAMPLE

Figure 11: Effect of pyrite addition to pellet on adhesion force and contact angle, oxidized mild steel substrate.

Figure 12: Effect of NaCl addition to the pellet on adhesion force and contact angle.

Figure 13: Pyrite drop adhesion force and contact angle as a function of substrate temperature.

Figure 14: Electron back-scatter image of perpendicular view of the drop interface, pyrite on oxidized mild steel: substrate temperature 500°C.

(a)

(b)

(c)

(d)

Figure 15: a) Secondary Electron Image of the substrate
b) Back-scatter image of the substrate of the same area as in (a)
c) Back-scatter image of the dark spotty region of the substrate as shown in (a) or (b).
d) Back-scatter image of the polished substrate of the same area as in (a) or (b).

STUDIES ON SLAG DEPOSIT FORMATION IN PULVERIZED COAL COMBUSTORS
PART II: RESULTS ON THE WETTING AND ADHESION OF SYNTHETIC ASH
DROPS ON DIFFERENT STEEL SUBSTRATES

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Introduction

In Part I⁽¹⁾ of this report, a test procedure was described in which small drops of synthetic coal ash slag were formed in a flame and dropped onto a steel substrate at a controlled temperature. The force of adhesion between the solidified drop and the substrate was determined by measurement of the force required to shear off the drop, and the minimum substrate temperature for adherence to occur was defined as the sticking temperature. The apparent contact angle of the drop on the surface was also measured. The results reported previously were primarily from studies of different compositions of synthetic ash drops on a mild steel substrate polished and preoxidized under a standard set of conditions. It was shown that adhesion involved a bonding to the oxide film on the steel substrate. In this report, the influence of variation of the substrate surface is investigated in more detail.

Experimental Techniques

The experimental apparatus used is shown in Figure 1a. It is similar to the apparatus described previously⁽²⁾, but modified to give greater consistency of results. The flame is produced from a three burner ring fed with a methane/oxygen mixture as shown in Figure 1b. The flow of each gas is controlled through needle valves and rotameters to be 870 ml/min of methane and 950 ml/min of oxygen, to ensure reproducible flame temperatures and melting conditions. The adiabatic flame temperature for this composition is $1770 \pm 20^\circ\text{C}$.

The substrate discs used previously were replaced with rectangular steel substrates 6.25 mm thick, 18.75 mm wide and 25 mm long, fitted into a groove cut in the center post of the bottom heater. The substrate was held in place by four screws and by loosening these screws it could be slid along to position a fresh portion of substrate surface beneath the drop path. Previously, the heating of the substrate was by conduction from the center post which was enclosed in a wire resistance heater coil. More uniform control at higher substrate temperatures was obtained by cementing an additional platinum wire heating element into a groove 3 mm deep by 14 mm wide cut into the bottom of the substrate.

The substrates tested were mild steel (SA 515) and 316 stainless steel. The standard polishing technique consisted of wet polishing with 400 grit Carbimet paper and water, followed by washing in acetone and drying. The standard oxidation conditions were 20 hours in an electric muffle furnace at 400°C in a steam of air. In some tests, an oxidized substrate was reduced in an electric furnace at 400°C under a flow of hydrogen. A series of oxidation conditions were examined on the two steels. In addition, mild steel substrates were coated with sodium silates using the freeze-drying technique described previously⁽¹⁾.

The synthetic coal ash mixture used contained 37% CaO , 23.7% Fe_2O_3 , 20.4% Al_2O_3 and 18.9% SiO_2 ground with a mortar and pestle. Cylindrical pellets 4 mm in diameter by 4 mm long, hanging from a platinum wire, were prepared as described by Moza and Austin⁽²⁾. It was found convenient to hand-hold the platinum wire with steel forceps, to position the pellets in the flame at a height of 5 cm above the substrate. The apparent contact angle and adhesion force of the solidified drop on the substrate at the controlled temperature were measured as before^(1,2). The strength of adhesion was indexed by the reading on a Metler E2000 balance (0 to 2000 g) when the drop was sheared off by a ram mounted on the balance.

Results

The initial mass of the synthetic ash pellet was 90 ± 5 milligrams (mg). This specific ash composition has a liquidus temperature of about 1480°C and readily falls from the platinum wire after melting, giving glassy ash spheres with a mass of 80 ± 5 mg. This represents a weight loss of about 11 percent of the original pellets mass. Thermogravimetric analysis (TGA) results indicated that the weight change was due mainly to the loss of two types of water. Adsorbed moisture accounts for a significant percentage of the pellet mass (~ 1.5) and is readily released as the pellet is rapidly heated in the flame. However, the primary source of the weight change was the structural water contained in calcium hydroxide ($\text{Ca}(\text{OH})_2$) which is formed during production of the pellets ($\sim 9.9\%$). A major portion of this water is released during the melting process.

A comparison of mild steel and stainless steel oxidized under standard conditions showed that drops stuck to the oxidized mild steel substrate at a minimum temperature of $465 \pm 5^\circ\text{C}$, the sticking temperature⁽³⁾, whereas they started to stick on stainless steel at $525 \pm 5^\circ\text{C}$ and above. The first part⁽¹⁾ of this report showed that the oxide layer on the mild steel was about $8 \mu\text{m}$ thick for preoxidation at standard conditions. The oxide layer is a very thin film on the stainless steel⁽⁴⁾. It has already been shown that the oxide layer plays an important role in the sticking behavior⁽¹⁾.

Figure 2 shows the apparent contact angle and force of adhesion as a function of substrate temperature for three preoxidizing conditions of the mild steel. The apparent contact angle changed drastically in the range of 350 to 500°C substrate temperature and became almost constant when sticking temperatures were reached. The sample which was not preoxidized showed a growth of oxide layer as the temperature approached 400°C . At 465°C , where sticking started to occur, the surface was fairly heavily oxidized and the difference in adhesion strengths between the preoxidized and non-preoxidized samples was not very great.

In the case of the stainless steel substrates, see Figure 3, the oxide film grew much more slowly during the period of the test for substrate temperatures less than 600°C and remained thin. The change in apparent contact angle with temperature was more gradual than on the mild steel, and the adhesion force for the non-preoxidized steel was low. The adhesion strengths on the preoxidized substrates were slightly higher up to 560°C than on the non-

preoxidized surface, but a very sudden increase occurred on the preoxidized steels over the temperature range of 560–600°C, giving adhesion strengths greater than the balance capacity at about 600°C. A gradual color change from amber to deep blue occurred on the stainless steel surface between 560 and 600°C.

The effect of the temperature of oxidation during the preoxidation of mild steel substrates for 20 hours is shown in Figure 4. The apparent contact angle at a given substrate temperature did not vary much for preoxidation temperatures of 300 to 450°C, but higher preoxidation temperatures produced a change in shape of the apparent contact angle versus substrate temperature curve. The sudden decrease at substrate temperatures of 350 to 500°C changed to a more gradual decrease up to 450°C. It was concluded that the oxide film grew more rapidly above 450°C and the enhanced growth gave better wetting of the substrate surface by a slag drop. Correspondingly, the sticking temperature for preoxidation temperatures showed a tendency to decrease and the adhesion strength to increase, the greatest changes occurring above 550°C. Figure 5 shows the same general trend in apparent wetting behavior when the preoxidation was carried out at 400°C but for longer times. For example, preoxidation at 400°C for 100 hours gave a curve of apparent contact angle versus substrate temperature which varied only from 110° to 90° over the range of 0 to 600°C. However, the adhesion force did not appear to be affected.

Contrary to the behavior on mild steel, increasing the preoxidation temperature of the stainless steel substrate had a more pronounced effect on the adhesion behavior and little effect on the apparent contact angle behavior, as shown in Figure 6. The sticking temperature/adhesion strength curve shifted to lower temperatures in a consistent manner as the preoxidation temperature increased. For example, the sticking temperature for the substrate preoxidized at 600°C dropped to $480 \pm 5^\circ\text{C}$ and the adhesion strength increased to over 2000 grams at 552°C. The scanning electron microscopy (SEM) images in Figure 7 show that the oxide layer on the surface preoxidized at 600°C (7b) is thicker and more porous than on the surface pretreated according to standard conditions (7a).

The effect of surface roughness of mild steel was investigated by polishing the surface with different size grits. Examination of the surfaces showed deeper polishing striations for the coarser grits. However, after standard oxidation the surface did not show significant differences in appearance because the oxide layer was relatively thick and had its own porosity which dominated over the polishing striations. Little effect was seen on the apparent contact angle and sticking force measured after preoxidation for mild steel polished with the different grits before oxidation. On the other hand, for roughened stainless steels the striations showed on the surface covered by the thin oxide film (see Figure 7a). At lower temperatures, the rougher surfaces gave much lower sticking temperatures, but with weak adherence ($\leq$ one gram). This was attributed to mechanical adhesion to the roughened surface. At higher substrate temperatures, above the normal sticking temperatures of 525°C, the adhesion strength was the same for all surface roughnesses, as shown in Figure 8. Again, a major increase in adhesion force was seen near 600°C.

A mild steel surface was also roughened by standard oxidation followed by partial reduction in H_2 at 400°C to create a roughened surface as shown in the SEM micrographs in Figure 9. Figure 9a is the oxidized surface; 9b is the surface after partial reduction; 9c is a back-scatter image of 9b.

where the white regions show unoxidized iron and the grey regions show iron oxide still remaining; 9d is a magnified region of 9b showing the large pores and fissures which developed on the surface during reduction. Figure 10 shows that the apparent contact angles were much smaller on the reduced surface, indicating much greater wetting on this surface at a given temperature. Also, the sticking temperature was decreased and the adhesion strength was increased. The difference between these results and those for the mild steel roughened by various grits was that the roughness produced by reducing the oxide film was much greater than the porosity of the oxide film itself. This result may explain the lower sticking temperature and higher adhesion strengths for a pretreatment environment containing CO and CO₂, see Figure 2, since this environment might have caused a similar surface development by oxidation/reduction processes.

It was shown before⁽¹⁾ that a coating of NaCl on the substrate caused major changes in the sticking behavior. This type of test was repeated using Na₂SO₄, with the results shown in Figure 11. The thickness of the deposited layer was varied by varying the concentration of salt dissolved in the liquid coating before freeze-drying. The apparent contact angle changed from about 150° at substrate temperatures of room temperature to 85 to 95° at temperatures above 550°C, for all tests. However, the major decrease in apparent contact angle occurred at lower temperatures for higher thicknesses of the deposited layer. Similarly, the entire sticking temperature/adhesion force curve was shifted to lower temperatures in a consistent manner. Figure 12 shows that Na₂CO₃ behaved similarly, with an even more pronounced effect on the sticking temperature.

SEM-microprobe examination of the surface-drop interfaces after shearing off the drop showed that some sodium sulfate was left on the oxidized steel surface, but a substantial amount was dissolved in the drop. Figure 13a is an SEM micrograph of the drop surface showing the regions of drop-substrate surface interaction of the Na₂SO₄ coated substrate. Figure 13b is a back-scatter image of the exposed steel where the oxide layer has been removed. It shows sulfur-rich regions (dark patches) in the steel, indicating that sulfur had diffused through the oxide layer into the steel beneath. Figure 13c shows that the pellet interacted with the Na₂CO₃-coated substrate in much the same manner as with the NaCl-coated substrate in the first report⁽¹⁾. All the sodium carbonate appeared to be absorbed by the drop. Figure 13d is a back-scatter image of the remaining surface. In both cases no sodium was detected in the exposed steel.

Discussion of Results and Conclusions

The apparent contact angle and sticking temperature-adhesion behavior can only be reproduced if the substrate surface is prepared in a standard manner. The oxide film which grows on mild steel affects the apparent contact angle, giving increased wetting at lower temperatures for any condition which thickens the film, such as higher preoxidation temperatures, longer preoxidation times, and substrate temperatures high enough for the film to form as the substrate is brought up to temperature. In general, increased wetting correlated with reduced sticking temperature, and sometimes with increased adhesion force.

The sudden increase in adhesion strength on stainless steel at about 600°C was probably due to a rearrangement of the surface oxide layer at this temperature. Darken and Gurry⁽⁵⁾ have shown that there is a major phase change in the iron-oxygen system at 560 to 570°C, see Figure 14. It can be expected that Wustite (FeO) became the predominant iron oxide in the oxide layer, particularly in the region adjacent to the metal surface. Interaction of the glass drop with the thicker FeO-rich layer adjacent to the steel surface led to greater adhesion strengths. This adhesion behavior is in agreement with enameling experience⁽⁶⁾, where a stronger chemical bond results from the presence of iron oxide in its lowest state of oxidation at the glass-metal interface. It has been proposed⁽⁴⁾ that the adhesion between the metal and FeO is also stronger. A transition from Fe to FeO, where the oxygen content increases gradually outwards through the film can result in a stronger bond between the metal and the oxide. This may also explain the increased adhesion strengths at lower substrate temperatures observed on mild steel preoxidized above 550°C (see Figure 4).

Creation of a more porous oxide layer decreased the apparent contact angle and increases adhesion strength. Alkali fluxes on the surface also increase the wetting at low substrate temperatures and increase the force of adhesion. There is substantial evidence for movement of iron and

It can be hypothesized that the spreading of a drop on the surface until it solidifies is a function of three major factors: (i) the surface tension between the drop and the surface, dependent on the chemical nature of the surface and the drop; (ii) the viscosity of the glass at the interface, dependent on the drop composition and how rapidly the interface is chilling and (iii) the physical state of the surface, that is, micro-capillary action. It seems likely that the presence of a layer of iron oxide will enhance spreading on all of these accounts, since iron oxide is more compatible with the inorganic oxides of the glass than bare metal, a layer of iron oxide reduced the rate of heat conduction away from the interface and keeps the glass less viscous for a longer time, and the oxide layer is microporous.

The adhesion force can also be postulated to depend on three factors: (i) the contact area as indicated by the apparent contact angle; (ii) chemical bonding between the glass and substrate; and (iii) mechanical keying produced by penetration and solidification of glass into micropores on the substrate surface. Again, it is likely that these three factors are, in general, enhanced by the presence of oxide films.

The presence of an alkali salt on the surface which absorbs into the drop interface will increase the adhesion strength by giving a less viscous glass and a lower solidification temperature and, hence, more spreading and a larger contact area. It might also increase the adhesion strength via effects (ii) and (iii), since the surface chemistry is altered, and the lower viscosity and lower solidification temperature might enhance the penetration of glass into the micropores.

To test whether the actual bonding mechanism is chemical or due to a mechanical keying action, or a combination of both, it is desirable to compare the results of adhesion on surfaces of similar microporosity, but oxidized in one case and completely reduced in the other. This experiment remains to be done.

Acknowledgements

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Figure Captions

- Figure 1a. Experimental apparatus (modified apparatus).
- Figure 1b. Experimental apparatus (three-burner ring).
- Figure 2. Variation of apparent contact angle and adhesion strength with oxidizing environment for mild steel substrate (SA 515).
- Figure 3. Variation of apparent contact angle and adhesion strength with oxidizing environment for stainless steel substrate (SS 316).
- Figure 4. Variation of apparent contact angle and adhesion strength with oxidation temperature for mild steel substrates.
- Figure 5. Variation of apparent contact angle and adhesion strength with time of oxidation for mild steel substrates.
- Figure 6. Variation of apparent contact angle and adhesion strength with oxidation temperature for stainless steel substrates.
- Figure 7. SEM micrographs of 316 stainless steel after pre-oxidation under a) standard conditions b) 600°C for 20 hours in air.
- Figure 8. Variation of apparent contact angle and adhesion strength with surface roughness for stainless steel substrates.
- Figure 9. Comparison of mild steel surfaces following oxidation/reduction reactions.
- a) SEI of oxide layer on mild steel after preoxidation under standard conditions
 - b) SEI of oxide layer on the same mild steel surface after subsequent reduction in hydrogen
 - c) BSI of some surface as shown in part 6, showing iron in both reduction (white areas) and oxidized (grey areas) states
 - d) SEI of an area of b magnified 10x showing fissures and pores on the roughened surface.
- Figure 10. Variation of apparent contact angle and adhesion strength with surface roughness by reduction of the oxide layer on mild steel substrate.

- Figure 11. Variation of apparent contact angle and adhesion strength with sodium sulfate coatings on oxidized mild steel substrates.
- Figure 12. Variation of apparent contact angle and adhesion strength with sodium carbonate coatings on oxidized mild steel substrates.
- Figure 13. Surface-drop interfaces for Na_2SO_4 and Na_2CO_3 coated substrates.
- a) SEI of interface on drop after reaction with Na_2SO_4 coated substrate
 - b) BSI of steel surface showing sulfur-high regions (dark patches)
 - c) SEI of drop surface after reaction with Na_2CO_3 coated substrate
 - d) BSI of steel surface.
- Figure 14. Temperature-composition diagram for the iron-oxygen system at one atmosphere.

Figure 1a. Experimental apparatus (modified apparatus).

Figure 1b. Experimental apparatus (three-burner ring).

Figure 2. Variation of apparent contact angle and adhesion strength with oxidizing environment for mild steel substrate (SAS 515).

Figure 3. Variation of apparent contact angle and adhesion strength with oxidizing environment for stainless steel substrate (SS 316).

Figure 4. Variation of apparent contact angle and adhesion strength with oxidation temperature for mild steel substrates.

Figure 5. Variation of apparent contact angle and adhesion strength with time of oxidation for mild steel substrates.

Figure 6. Variation of apparent contact angle and adhesion strength with oxidation temperature for stainless steel substrates.

a)

b)

Figure 7. SEM micrographs of 316 stainless steel after preoxidation under a) standard conditions b) 600°C for 20 hours in air.

Figure 8. Variation of apparent contact angle and adhesion strength with surface roughness for stainless steel substrates.

a)

b)

c)

d)

Figure 9. Comparison of mild steel surfaces following oxidation/reduction reactions.

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a)

b)

c)

d)

Figure 13. Surface-drop interfaces for Na_2SO_4 and Na_2CO_3 coated substrates.

- a) SEI of interface on drop after reaction with Na_2SO_4 coated substrate
- b) BSI of steel surface showing sulfur-high regions (dark patches)
- c) SEI of drop surface after reaction with Na_2CO_3 coated substrate
- d) BSI of steel surface.

Fe-O

Figure 14. Temperature-composition diagram for the iron-oxygen system at one atmosphere.

STUDIES ON SLAG DEPOSIT FORMATION IN PULVERIZED COAL COMBUSTORS
PART III: A PRELIMINARY HYPOTHESIS FOR THE STICKING BEHAVIOR OF
SLAG DROPS ON STEELS

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Introduction

In Parts I and II of this report^(1,2), results were given on the adherence of molten synthetic coal ash drops on steel substrates, and the effect of surface treatment of the substrate on the adhesion phenomenon. The results indicated that although the interface between the molten drop and the substrate solidified within a few milliseconds of contact there is transfer of chemical components between the drop and the surface. This transfer establishes a bond between the oxide film on mild steel and the glass. In this section, a mechanism is postulated to explain the effects of drop composition and substrate temperature on the formation of this bond.

Effect of Liquidus Temperature of the Pellet

In order to study the effect of the liquidus temperature of the drop, the simple oxide system $\text{CaO-Fe}_2\text{O}_3$ was chosen for the following reason: the surface layer of an oxidized mild steel substrate is primarily Fe_2O_3 and therefore any interaction between the surface and the drop still creates a two-component system of accurately known liquidus temperature⁽³⁾. Pellets made from mixtures of powdered $\text{CaO-Fe}_2\text{O}_3$ were tested on a high carbon steel substrate ($\text{C} = 0.44$, $\text{Mn} = 0.8$, P and S less than 0.4 weight %). This was oxidized at 400°C for 20 hours, followed by further oxidation for two hours at 580°C to develop a predominantly Fe_2O_3 surface⁽⁴⁾. All the pellets were melted under identical flame conditions. The temperature at which the drop just sticks (the sticking temperature) was measured by incrementing the substrate temperature in steps of 10°C , with a fresh drop for each increase. The results are shown in Figure 1.

The apparent contact angle at the sticking temperature decreases as the iron content increased, indicating improved wetting. The sticking temperature passed through a minimum at a pellet composition of 65% Fe_2O_3 and 35% CaO . The liquidus temperature of the $\text{CaO-Fe}_2\text{O}_3$ system is also plotted. The curves indicate that sticking temperature follows a similar trend to that of liquidus temperature, except that the minimum occurs at a lower iron content, that is, the sticking temperature is shifted somewhat to the left in comparison to liquidus temperature, to lower Fe_2O_3 content. The comparative shift between the compositions for minimum liquidus and sticking temperatures suggests that the interface had absorbed about 15% of Fe_2O_3 . Sticking occurs better at a lower liquidus temperature because the time for the interface to solidify is then extended, thus increasing the reaction time of molten slag in contact with the oxide layer.

To further study the effect of the sticking temperature of pick-up of Fe_2O_3 from the iron substrate, two compositions of the $\text{SiO}_2\text{-CaO-Fe}_2\text{O}_3$ system were tested. These two were chosen because the liquidus temperature was the same for each beginning composition. The results are shown in Table 1. The results showed that the sticking temperature was lower for the case in

Table 1: Effect of Fe_2O_3 pick-up from the substrate on the sticking temperature.

Composition, Weight %			Sticking	Liquidus	Effect of added Fe_2O_3 on liquidus temperature
SiO_2	CaO	Fe_2O_3	Temperature $^\circ\text{C}$	Temperature $^\circ\text{C}$	
33	28	39	368	1300	Increase
33.3	33.3	33.3	327	1305	Decrease

which further addition of Fe_2O_3 would reduce the liquidus temperature. Thus, if the composition of the fly ash drop is such that it can be fluxed by the oxide on the boiler tube surface, better sticking of the ash particle results. In such a case the interface between droplet and metal remain molten for a longer time as compared to the non-fluxing case.

Effect of Iron Oxide Concentrations in the Pellet

A starting mixture of 57% CaO and 43% SiO_2 was chosen because additions of up to 20% weight Fe_2O_3 to this mixture would not alter the liquidus temperature by more than 50°C ⁽⁵⁾ and the liquidus temperature of the mixture is around 1550°C , so that it can be easily melted in the test flame⁽¹⁾. The mild steel substrate was the same as before, pre-treated in the same fashion to get a predominantly Fe_2O_3 layer at the surface. The results for the cases with no Fe_2O_3 , 2.5% Fe_2O_3 and 9.5% Fe_2O_3 in the pellet are shown in Figure 2. Sticking temperatures were almost the same, and strength curves followed similar trends for the three cases. Up to about 400°C , apparent contact angles were somewhat lower for pellets with 9.5% Fe_2O_3 . Figure 3 shows a plot of sticking temperature with respect to Fe_2O_3 content in these pellets. The liquidus temperature of the various compositions⁽⁵⁾ is also plotted in the same figure. The sticking temperature did not change drastically with increasing Fe_2O_3 content in the pellet, showing no strong chemical effect independent of liquidus temperature in this particular test. Increasing Fe_2O_3 to 20% in the pellet (not shown in the curve) altered the sticking temperature significantly as expected, corresponding to a change in the liquidus temperature.

Solidified drops from the set of experiments where drops contained no iron (composition 57% CaO and 43% SiO_2) were saved for depth profile analysis by ion beam spectrochemical analysis⁽⁶⁾. In this method the surface is bombarded by a high energy ion beam and the energy and quantity of released photons is used to identify and measure the atoms sputtered from the surface. Since sputtering involves exposing fresh surface each time, it is possible by recording the intensity of photons corresponding to a certain element with respect to time to get a depth profile of that element in the surface. Figure 4 shows such a profile for Ca, Fe and Si through the drop surface that had come in contact with the metal substrate (substrate temperature 500°C). It was concluded that near the surface the drop had mostly a layer of iron oxide picked up from the substrate, followed by an interfacial region of about 5 micrometers thickness, followed by the bulk of the drop containing no iron. The thickness of the interfacial region was found to be a function of the substrate temperature, as shown in Figure 5. In this figure the interfacial region was defined as the region where the normalized intensity of each of the three elements Ca, Si and Fe is at least 0.1: the scatter in the data is attributed to experimental error. As the substrate temperature was increased, the thickness of the interfacial region increased. This indicates an increase in mass transport of species at the interface as the substrate temperature was increased.

Theoretical Considerations of Heat Transfer

The drop-metal interactions may be treated as a case of liquid slag coming into contact with a metal surface, with slag solidification progressing up through the slag drop⁽¹⁾. Figure 6 shows an exaggerated view of the system, simplified to make it amenable to analysis. The following assumptions were made: at time $t=0$, the region $x<0$ is solid and $x>0$ is liquid; at time t , an interfacial region of thickness X is developed between solid metal and liquid. This solidified region might have a different composition than the liquid, but it was assumed for simplicity to have the same composition. The region $x<0$ is initially a solid of thermal constants K_S , ρ_S , c_S , α_S and is at temperature T_S (substrate temperature) and the region $x>0$ is initially liquid of thermal constants K_L , ρ_L , c_L , α_L and at constant temperature T_L . The thermal constants of the solidified liquid are K_I , ρ_I , c_I and α_I , where the symbols K , ρ , c and α stand for thermal conductivity, density, specific heat and thermal diffusivity ($= K/\rho c$) respectively, and subscripts S , L and I stand for solid, liquid and interfacial regions respectively.

The solution⁽⁷⁾ for this simplified model relates the thickness of solidified interfacial region X with time t and has the form

$$\frac{K_S \alpha_I^{1/2} e^{-\lambda^2}}{K_I \alpha_S^{1/2} + K_S \alpha_I^{1/2} \operatorname{erf} \lambda} + \frac{K_L \alpha_I^{1/2} (T_L - T_{MP}) e^{-\lambda^2 / \alpha_L}}{K_I \alpha_L^{1/2} (T_{MP} - T_S) \operatorname{erfc} [\lambda (\alpha_I / \alpha_L)^{1/2}]} = \frac{\lambda H \pi^{1/2}}{c_I (T_{MP} - T_S)} \quad (1)$$

where H is the latent heat of fusion for the interface material of liquidus temperature T_{MP} and

$$\lambda = \frac{X^2}{4 \alpha_I t}$$

This solution applies for the solid metal side and liquid drop side effectively infinite in both directions, so that the temperature of solid metal and liquid drop can be treated as constant with time. This assumption would be valid for a short time after the impact of the drop with the interface.

All the parameters in Equation 1 can be estimated for a fixed system, with the variables being X and t . In the system analyzed, the substrate was iron, and the slag had a composition of 20.4% SiO_2 , 18.9% Al_2O_3 , 23.7% Fe_2O_3 and 37% CaO (1). The value of the various thermal constants are given in Table 2, where literature values of thermal conductivity and density of the substrate for a range of temperatures were fitted to first order polynomials in temperature, and the liquid slag values were estimated based on the mole fraction weighted sum of values for each component. The value of T_L was chosen to be 1750°C , which is the approximate temperature at which the drops fall from the platinum wire. The value of T_{MP} for the above slag would be 1460°C and the estimate of H was 179 cal/g. The metal substrate temperature T_S was chosen from 0 to 650°C in steps of 50°C . Equation 1 was solved for t , for certain fixed values of X . Choosing X as $1\mu\text{m}$, $2\mu\text{m}$ and $5\mu\text{m}$, t was calculated by a numerical trail-and-error search for λ , for different values of T_S .

To show the effect of liquidus temperature, all the above values were used but T_{MP} was varied. Typical results are plotted in Figure 7 for a liquidus temperature of 1200°C and indicate that, as expected, as substrate temperature is increased it takes longer time for a certain thickness of frozen interface to be formed. In other words, the interface remains molten for a longer time as the substrate temperature is increased. The value of the thermal constants were varied over the ranges they are expected to vary in practice (approximately $\pm 20\%$ from mean). The effect on t for X equal to $2\mu\text{m}$ was found to be negligible, that is, the time for which an interfacial region of two micrometers thick remains partly fluid is not sensitive to small variations in the thermal constants of metal, interfacial material or the liquid slag. Similar results were found by varying the initial temperature of the slag between 1600°C and 1800°C . In all of these calculations, each parameter was varied independently while keeping all other variables constant.

The effect of varying the liquidus temperature from 1960°C to 800°C had a profound effect on the freezing time, particularly at higher substrate temperature. The results are plotted in Figure 8. In these curves the thickness of the interfacial region was fixed at $2\mu\text{m}$, since the ion sputtering studies had indicated this to be the approximate thickness of the interfacial region at the sticking temperature. The curves indicate that at a substrate temperature of 460°C the time that it takes for the interfacial region of $2\mu\text{m}$ thick to solidify is $16\mu\text{sec}$, $130\mu\text{sec}$ and $1900\mu\text{sec}$ for liquidus temperatures of the interfacial regions of 1400, 1200, 1000 and 800°C respectively.

It should be remembered that liquidus temperatures are equilibrium temperatures whereas the contact zones under study become rigid in milliseconds. The interfacial region treated here as solidified slag is more likely to exist initially as a supercooled liquid of high viscosity. However, this concept does not alter the validity of the general reasoning or the heat transfer calculation.

Table 2. Thermal properties of materials.

	Thermal conductivity cal/sec cm °C	Specific heat cal/gm C°	Density g/cm ²
Substrate ⁽⁸⁾	$0.166-(1.24)(T)(10^{-4})$	0.1075	$8.37(0.8)(T)(10^{-3})$
Liquid slag ⁽⁹⁾	0.01	0.2	3.53
Interfacial ⁽¹⁰⁾ region	0.0025	0.25	2.50

Discussion

It appears probable that in order for a strong bond to form between the drop and the oxide film on the substrate it is necessary to form an interfacial region consisting of both iron oxide and slag. The formation of this region is assisted by long times of contact of liquid slag with the substrate, during which time interchange of components occur, since such reactions will be very slow in a solid-solid system at the relatively low substrate temperatures of 600°C and less. The heat transfer calculation, although over simplified, clearly indicates that higher substrate temperature and lower liquidus temperatures greatly increase the time to solidify a 2 μ m thick interface, and the experimental results also verify that the thickness of the interface increases with higher substrate temperatures. A slag composition which has a low liquidus temperature, or one for which the liquidus temperature decreases as it picks up iron will tend to stick more readily to the substrate.

The apparent contact angle measured in this type of test is not an equilibrium contact angle because of the short times of liquid-solid contact. It represents the wetting, spreading and flattening of a drop during the time of freezing of the contact. It is not surprising, therefore, that low substrate temperatures tend to give high contact angles because they reduce the time of solidification. A low contact angle is probably due to a combination of low surface tension, low viscosity and long solidification times. Low apparent contact angle does indicate more wetting and a wider area of contact, therefore additional bond strength. In addition, the bond may be partially formed by penetration of slag into micropores in the substrate surface⁽²⁾. In this case, penetration is also aided by low surface tension, low viscosity and long solidification times.

There is obviously an additional role of the chemistry of the slag drop composition and the substrate surface, besides their effects on liquidus temperature. A comparison of Figures 1 and 3 shows that at identical liquidus temperatures the sticking temperatures are not identical. For instance at a liquidus temperature of 1510°C, Figure 3 indicates the sticking temperature to be around 425°C for the system SiO₂-CaO-Fe₂O₃ whereas Figure 1 indicates the sticking temperature to be 510°C for the CaO-Fe₂O₃ system. It is well-established⁽¹²⁾ that oxide-base glasses do not readily wet unoxidized metal surfaces, probably because the electronegative surface of the metal is repulsive to the electronegative surface of oxide anions⁽¹³⁾. It may be hypothesized that different chemical compositions have different sticking temperatures because of the following possibilities. First, the chemical rate of transfer of iron to the glass and the consequent bond formation to the iron oxide may be different for different glass compositions. Second, the surface tension and viscosity may be different. Third, the coefficient of thermal expansion of the glass versus the metal oxide may be different, which will affect the stress developed during cooling. Each of these factors requires further investigation.

Table 3 shows surface tensions of iron containing traces of sulfur, pyrrhotite and Fe_2O_3 . Our previous results⁽¹⁾ showed that drops of pyrrhotite formed from melting pyrite gave sticking at low substrate temperatures.

Any compound on the surface which fluxes the interfacial region as it is absorbed into the substrate-drop contact will tend to aid sticking via lowering the liquidus temperature and possibly reducing the surface tension and viscosity. Any compound which raises the liquidus temperature, increases the surface tension and viscosity or makes the drop interface chemically incompatible^(12,13) with the substrate will tend to prevent sticking. In addition, it is possible that a compound which promotes rapid crystallization in the interfacial region might also greatly reduce the bond strength.

It must be noted that the studies reported in these three papers are only concerned with the initiation of a slag deposit, that is, with the ability of drops to adhere to a clean oxidized steel surface. The slag deposit problem in general contains many other factors such as the addition of further drops onto the initial layer, the sintering of the total deposit to make it strong, the relative coefficients of expansion of slag deposit and metal which determines whether thermal cycling can crack off the deposit, and so on.

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Table 3. Surface Tensions of Some Iron Sulfur Compounds⁽¹¹⁾.

Material	Temperature °C	Surface tension dynes/cm
Fe (0.04%S)	1550	1788
Fe (0.1%S)	1550	1200
FeS	1450	340
Fe ₂ O ₃	1420	590

Figure Captions

- Figure 1. Slag drop sticking temperature and contact angle as a function of liquidus temperature of the drop.
- Figure 2. Slag drop adhesion force and apparent contact angle as a function of increased amount of Fe_2O_3 in pellets of Fe_2O_3 added to 57% CaO 43% SiO_2 .
- Figure 3. Slag drop sticking temperature as a function of Fe_2O_3 content in the pellet.
- Figure 4. The profile of Ca, Si and Fe from the interface into the drop for a drop of CaO and SiO_2 (by ion sputtering); substrate temperature 500°C .
- Figure 5. Thickness of the interfacial region containing iron as a function of substrate temperature.
- Figure 6. Illustration of unsteady state temperature profiles through metal-drop interface after contact.
- Figure 7. Typical results of variation of time to form a solidified interface $X \mu\text{m}$ thick: liquidus temperature of the interface $T_{\text{MP}} = 1200^\circ\text{C}$.
- Figure 8. Typical results of variation of time to form a solid interface $2 \mu\text{m}$ thick as a function of the substrate temperature of the interface.

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Figure 8. Typical results of variation of time to form a solid interface $2\text{ }\mu\text{m}$ thick as a function of the substrate temperature of the interface.

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SECTION 3. THE STUDY OF SLAG DEPOSITS IN A LABORATORY PULVERIZED COAL FURNACE

3.1. Experimental Techniques

3.1.1. The Furnace

Figures 6, 7, 8, 9 and 10 of section 1.5 (pages 16-22) show the general design of the furnace which had previously been used at The Pennsylvania State University for studies of combustion in pulverized coal flames⁽¹⁾. This furnace was designed to give safe operation for pulverized coal pre-mixed with cold air to produce a plane flame, that is, a residence time distribution corresponding to close to plug flow with no back-mixing into the flame. Essentially, the furnace consists of a p.c.-air premixer and burner, a down-fired vertical combustion chamber and an uprising refractory leg connected to a steel stack.

The premixer-burner is situated on the top of the combustion chamber. It receives the mixture of fuel plus primary conveying air, mixes it thoroughly with the secondary air and disperses the mixture in a plug flow manner. The shape of the premixer-burner is a truncated pyramid of square cross-section whose base is fitted onto a two row bank of water-cooled copper tubes. The pyramid expands downwards with an angle 10.6° between the center line and its sides. The dimensions of the base resting on the top of the water cooled tubes are 6.5"x6.5". The pyramid is constructed of stainless steel plates which are bonded together with high temperature air setting mortar (Franset, J. H. France Co.). The pyramid is easily removable for inspection of the interior of the furnace.

The water tube bank consists of two rows of horizontal tubes. The tubes in each row are one outside tube diameter apart and rows are separated vertically by about one inch. The top of each tube is fitted with a stationary vane of triangular cross-section which tapers from base width equal to the outer diameter of the tube to a sharp peak located about one inch above the center line. The vanes prevent the accumulation of coal dust on the top of the tubes and direct the flow of coal particles through the bank with minimum turbulence. The two rows of tubes are staggered in such a fashion that the empty spaces between the tubes in a row are in exact vertical alignment with the tubes of the other row. This arrangement makes the tube bank function as an efficient radiation shield, yet still allows the coal particles to pass through. The water-cooled tube bank forces the flame to stabilize at the desired position and it prevents the flame from flashing back into the premixing zone. The tubes are of 1/4" thick copper wall while the vanes are constructed of 24 gauge galvanized sheet soft silver soldered onto the tubes. Water flow is commenced before the furnace is fired, obviously, and maintained at the end of a

test until the furnace is cool, to prevent melting of the silver solder.

The combustion chamber consists of four vertical walls constructed of insulating refractory bricks, bonded together with high temperature mortar. The bricks are composed of 50% alumina and 50% silica, and can withstand up to 1530°C temperature. The height of the vertical combustion chamber is approximately 335 cm, interior cross-section area is 6.5" square (16.51 cm) and the thickness of the walls is 5" (12.7 cm). The height of the combustion chamber was increased from 226 cm to 335 cm to achieve longer coal particle residence time, and the wall thickness was increased from 6.35 to 12.7 cm to reduce heat loss. The combustion chamber is encased with 3/8" thick transite sheet to reduce heat loss and eliminate air leakage.

The sampling ports on the front side wall of the furnace are kept closed during the furnace operation, using ceramic plugs. The junction between the uprising flue and the combustion chamber is located at a short distance above the bottom of the chamber in order to collect unburned material at the base. The flue is constructed of the same type of bricks and mortar as used for the combustion chamber, but of a single layer thick (6.35 cm).

The air supply system consists of a primary air line and a secondary air line. The primary air line supplies compressed air (80 psi) for the coal ejector (see later) and the secondary air line supplies low pressure air, produced by a blower with a capacity of 350 SCFM. A 2" gate valve in the secondary air line controls the flow of air. The primary and secondary air lines are connected to two rotameters (Schulte and Koerting Co., 0-25 SCFM, 0-30 SCFM) respectively. The total flow rate of combustion air is controlled by adjusting the required total flow through both primary and secondary air lines.

The coal feeder system consists of a large primary hopper, a small secondary hopper, a vibratory feeder, and a venturi ejector for introducing the coal into the primary air, which is then pneumatically carried to the premixer-burner. The venturi device is composed of a funnel whose spout is fitted into the throat of a assymmetric venturi. The funnel is made out of brass and the venturi is made by cutting and sealing a notch in a 3/8" stainless steel tube. The upstream and downstream of the notch are cut at angles respectively of 60° and 12° to the axis of the tube, and to a depth of about 2/3 of the diameter of the tube. The funnel is soldered into an opening left in the throat of the venturi. With the unit installed in the primary air line, the flow through the venturi creates a suction at the spout of the funnel which is sufficient to allow pulverized coal to be pulled from the funnel into the air line by atmospheric pressure. Figure 1 shows the details of the ejector.

Figure 1. Details of ejector.

To measure the furnace inner wall temperatures twelve thermocouples are connected to a 24-point Leeds and Northrup "Speedomax G" temperature recorder which scans the twelve thermocouples once every 24 seconds. The thermocouples are fixed along the longitudinal center line of the right side of the combustion chamber. The thermocouple wire (0.128" diameter Pt/Pt-10% Rh) is insulated with alumina double-bore tubing (.0126" O.D. x 0.0233" I.D. x 6" long) and installed in an alumina protecting tube (0.218" O.D. x 0.150" I.D. x 6" long) with one end closed.

Before the start of a test, the steel stack is heated with a gas burner located at the base to create natural draft conditions (30-45 minutes). During this time, the coal feeder is calibrated by collecting test coal over timed periods and weighing the coal.

The furnace is raised in temperature before the start of firing with coal by means of a water-cooled gas burner (see Figure 2) inserted in the top of the furnace below the tube bank. A small gas flame is used initially, with a low air flow through the tube bank, and as the furnace enclosure becomes hotter more gas and air are supplied at a rate less than flame failure, until full burner capacity is reached. When the wall thermocouples reach 500°C or above, a small amount of coal is fired and the rate gradually increased until the wall thermocouples record 1000°C. The gas burner is then shutoff, removed, the hole plugged and a desired steady coal feed established. After an hour of coal firing the temperature was almost constant and tests were run in the next four hours of operation.

The following precautions were considered important for safe and correct furnace operation:

1. The coal feed rate must be recalibrated for each type of coal used.
2. The funnel attached to the venturi should be checked periodically, since blockage of the nozzle can occur due to larger coal particles or foreign material.
3. Before the furnace is fired, water must be passing through the water tube banks.
4. The furnace wall temperature must be checked periodically to confirm the presence of the flame.
5. Material must be removed every 30 minutes from the bottom of the furnace and stack, in order to prevent pressure build-up in the furnace.
6. Before any actual test is conducted, steady state temperature must be obtained.

Figure 2. Gas burner.

7. After the experiments are finished, the air and feeder lines must be first turned off. The water, however, must run through the water tube banks for the following night so that the furnace may cool down without damage to the mixer-burner.
8. The high pressure gas line must be turned off at the main.

Furnace gas temperatures were measured with a water-cooled suction pyrometer, where flue gas is pulled at high velocity over a shielded thermocouple, as shown in Figure 3. It consists of a Pt/Pt-10% Rh thermocouple which is placed into a two-bore ceramic tube. The head of this tube is protected by another ceramic tube (O.D. 19"/64, I.D. 13"/64 and 8" long) with one end closed. This whole assembly is covered by an open-ended ceramic shield tube and gas is sucked through the annulus. This head is supported on a water-cooled body composed of two concentric copper tubes through which water is circulated to cool the hot gases after they have passed the thermocouple head. The suction pump has a capacity of 0.2 CFM.

3.1.2. Characterization of the Furnace

The velocity profile of cold air through the furnace is shown in Figure 4 at a mean velocity of about 1 foot measured with a hot-core anemometer. The result indicates no reversal of flow and, therefore, no macro back-mixing, with a relatively flat velocity profile across most of the region.

Figure 5 shows the wall and gas temperature measurements for Illinois #6 coal (39.2% volatile matter, DAF), at approximately stoichiometric air-coal ratio. It was concluded that the peak wall temperatures could be used as a reasonable index of peak flame temperature by adding 157°C. The maximum temperature occurred at about 50 cm from the tube bank, but was less than 1400°C. Figure 6 shows the result for the lower volatile Upper Freeport (Keystone) coal (28.7% V.M. DAF). In this case, the maximum flame temperature was about 1420°C at 140 cm from the tube bank, representing a slower igniting coal. The heat loss rate was about 100°C per 100 cm of furnace length. It was also found that a slow and relatively small increase of temperature occurred over several hours of operation, presumably due to heat conduction down the furnace walls. It was concluded that the small flame width was leading to somewhat low flame temperatures.

An electrically heated secondary air preheater was constructed to raise the temperature of the secondary air, as shown in Figure 7. The result is given in Figure 8 for Pittsburgh Sea coal (34.2% V.M. DAF). Preheating by 140°C only produced about 30-40°C increase in flame temperature. This is because the preheater gas-coal mixture flows through the water-tube bank which acts as an efficient heat removal exchanger. It was also noted that the Pittsburgh Sea Coal gave somewhat lower peak wall temperatures than the other two coals.

Figure 3. Schematic of suction pyrometer.

Figure 4. Flow velocity profile of cold air across the furnace ($0.40 \text{ m}^3/\text{min}$ at 25°C).

Figure 5. Wall and gas temperature profile versus distance from the tube bank for Illinois #6 Coal (10 lb/h).

Figure 6. Wall temperature and gas temperature versus distance from the tube bank for Keystone Coal (10 lb/h).

Figure 7. Secondary air preheater.

Figure 8. Comparison between temperature profiles for ambient and preheated (140°C) combustion air. Pittsburg Sea Coal (10 lb/h).

Figure 9 shows a typical result with varying levels of excess air. It is concluded that excess air in the premixed coal-air flow leads to higher gas velocity, an extension of the flame, and lower peak temperatures. Best results were obtained with stoichiometric air. Figure 10 shows the effect of coal rate: the flame was quite stable at 5 lb/h, but heat loss reduced the peak flame temperature by about 160°C.

The effect of enriching the air with O_2 was investigated. Figure 11 shows the result, for air with approximately 30% O_2 instead of 21%. The peak temperature was shifted closer to the burner due to more rapid ignition, but the peak temperature was not much increased.

To study the effect of fineness of the coal on the flame properties, the furnace was fired with Pittsburgh Sea coal having two degrees of fineness (see Table 1) keeping coal feed and air rates constant. The temperature distribution along the furnace axis indicated that increased fineness yielded a higher peak temperature and shifted the flame back to the tube bank, see Figure 12.

It was concluded that the design of furnace was not adequate to allow any simple means of obtaining the target of peak flame temperature of 1500 to 1550°C. However, the furnace was used to develop test probes and technique, as discussed next.

3.1.3. Development of Deposit Probes

Figure 13 shows the first design of deposit probe. It consisted of a semicylindrical piece of stainless steel attached to the probe surface as the substrate to collect the slag deposit, and a thermocouple inserted in the substrate to measure the temperature. In order to control the surface temperature, compressed air was used as a coolant entering through the inner tube and leaving from the annulus. The tests of this probe inside the furnace at the 1200°C gas temperature region showed that (i) it was difficult to control the temperature of slag-collecting metal piece within an accuracy of $\pm 5^\circ\text{C}$, (ii) the surface area of the substrate was insufficient to collect enough slag deposit to run the desired chemical analyses, (iii) it was difficult to remove the metal piece from the probe in order to analyze the slag deposited on the metal substrate.

A water-cooled metal probe was then developed in which molten ash particles are collected onto a metal substrate incorporated with the probe, as shown in Figure 14. The probe consists of two concentric stainless steel tubes, with an inside tube of 1/4" I.D. and 3/8" O.D. and an outside tube of 1/2" I.D. and 5/8" O.D. There are three major components attached to the probe: a metal substrate, a 1/16 inch chromel-alumel thermocouple and temperature recorder, and a precision water flow meter. Figure 14 shows a

Table 1. Screen analyses of Pittsburgh Sea Coal.

Mesh #	First sample wt.% < size	Second sample wt.% < size
100	97.6	76.0
140	88.6	68.0
200	75.6	56.0
270	60.60	42.40
400	51.60	34.80

Figure 9. Wall temperature profiles at different air to fuel ratios for Keystone coal (10 lbs/h).

Figure 10. Flame stability test for different firing rates, Pittsburgh Sea Coal.

Figure 11. Furnace wall temperature versus furnace length with O_2 injection for Keystone coal (10 lb/h).

Figure 12. Effect of the particle size distribution on wall temperature profiles: Pittsburgh Sea Coal (10 lb/h).

Figure 13. Air-cooled slag collection probe (Morris).

Figure 14. Water cooled slag deposit probe system.

schematic of the substrate attached to the probe. However, at a later stage of experimental observation, it was found necessary to construct a second type of substrate-probe configuration to give a closer temperature control, as shown in Figure 15. Since the substrate in this model is directly in contact with water flowing through the probe, the temperature control was more precise. This type of probe was necessary when substrate temperatures were controlled in the low end of the desired range, that is, in the region of 200 to 400°C.

An optical system consisting of a cathetometer and a Polaroid camera was set up to view the probe test area through a 2 inch diameter hole on the side wall. The build-up of the slag deposit was shown by photographs of the substrate surface taken 5 and 30 minutes after insertion of the probe. However, there were heat losses due to air leakage through the hole and due to these heat losses the gas temperature dropped substantially and it was not possible to control the temperature of the test substrate while viewing was performed.

3.1.4. Ash Balance

A first attempt at an ash balance was performed using Pittsburgh Sea Coal. The ash, slag and unburned coal were collected at the base of the furnace and base of the stack for one hour under three different conditions, stoichiometric, 10% excess air and -10% excess air (reducing conditions) at a coal feed rate of 10 lb/h. A sample was ashed according to the ASTM method to determine combustibles. Sampling of the particulate in the flue gas was carried out with the dust sampling probe developed by Howard(1), which consisted of a sampling tube with water jacket, a cyclone and a filter chamber, see Figure 16. The flue gas (at about 650°C temperature) at the upper section of the riser leg to the stack was sampled at a suction rate of 34 ml/minute, for 10 minutes, which gave a sampling velocity at the probe entrance of about twenty times the gas velocity in the furnace. The high suction velocity was necessary to prevent blockage of the tube.

The dust concentration in the flue gas was estimated from $C = M/A$, where C is in g/m^3 , M is the mass of dust collected in g and A the flue gas volume sampled in m^3 . The results are tabulated in Table 2. Using the values of C as the best available estimate at the present time, the estimated percentage distribution of the ash and slag was approximately 16 to 27% collected at the base of the furnace, 0.3 to 2.5% leaving as fly ash in the gas in the riser leg to the stack and 73-82% as wall slag. Obviously, the balance is too crude to be considered as a reasonable estimate, although the design of the furnace does lead to a large wall area collecting slag for a relatively small volume of flame.

3.2. Analysis of Deposition

A technique was developed for qualitatively following the build-up of deposit on the probe. It consisted of first establishing a controlled sub-

Table 2. Ash balance.

	Air	Flue Gas	Furnace Base					
	Nm ³ min	Nm ³ Q _f /min	Total Recovery of materials, W _t , g/min	Loss on Ignition L ₁ , %	Recovery of Ash and Slag W _a , g/min	Particulates in Flue gas to Stack C _s , g/Nm ³	Build-up of [*] Wall Slag W _s , g/min	Combustion ^{**} Efficiency η, %
1	0.54	0.52	2.14	50.5	1.06	0.39	5.34	98.4
2	0.60 (stoichiometric)	0.58	4.48	61.2	1.74	0.08	4.74	96.3
3	0.66	0.64	3.33	59.9	1.34	0.64	4.99	95.2

* Build-up of wall slag is estimated from

$$W_s = \left(\frac{\text{Percent Ash Content}}{100} \right) \times (\text{Coal Feed Rate}) - W_a - Q_f \times C_s \times (100 - L_1)/100$$

** Combustion Efficiency is defined as

$$= 100 \times (1 - L_1/100) \times (W_t + Q_f \times C_s) / \text{Coal Feed Rate}$$

Figure 15. Water cooled slag deposit probe system.

Figure 16. Solid-sampling probe (Howard).

strate temperature with the substrate shielded from collision by fly ash, by suitably adjusting the water flow through the probe. Then the probe was turned to bring the substrate into the stream of particles. Once initiation of deposit occurred, the growth of a layer of deposit led to reduced heat transfer and a fall in the temperature recorded by the thermocouple in the substrate. Figure 17 shows a typical result. It is clear that the initiation and growth of deposit depends on the substrate temperature.

Attempts were made to analyze the chemical nature of the deposit at initiation. However, in situ analysis using the electron microprobe gave results dominated by the material of the substrate, while removal of the deposit gave too little material for analysis. A systematic study of various coals, coals enriched with possible bad actors, etc., was not performed because it was felt that the furnace design needed modification before really meaningful results could be obtained (see next section).

3.3 Conclusions and Future Work

The existing furnace and collection system suffers from three major disadvantages. First, the furnace was originally designed by Essenhigh and Howard to study carbon burn-out, so it emulates a one-dimensional track along a flame. In doing so, however, it creates a long thin flame which has a large surface area of containing walls per unit volume, and, hence, high heat losses to the containing walls. This prevents the attainment of the target flame temperature, which makes results as far as slag drop formation concerned somewhat meaningless. The premixed nature of the coal-air feed means that high air preheat cannot be used, because of the danger of flash back and explosion in the feeder. Second, for identical reasons, the design may well lead to excessive stripping of slag drops from the flame by the containing walls, before the gas temperature decreases to the level corresponding to industrial furnace exit temperatures. Third, the design is not amenable to in situ viewing of the initiation of the deposit.

It is proposed in the next phase of this program to develop a furnace design to overcome these problems, before the techniques of analysis developed so far are applied in a systematic study of deposit initiation.

Reference - Section 3

1. Howard, J. B., "Mechanisms of Ignition and Combustion in Flames of Pulverized Bituminous Coal", Ph.D. thesis in Fuel Technology, 1965.

Figure 17. Typical substrate temperature versus deposition time. Illinois #6 coal pre-treated mild steel substrate.

APPENDIX IFLUORESCENCE CORRECTION FOR Al, Si, S AND Caa) ALUMINUM

Al is fluoresced by Si, S and Ca. Fe does not fluoresce Al, since it does not meet the criteria outlined in equation 2-19.

The following table gives the values of various parameters necessary for applying fluorescence correction to Al K α x-ray counts, using equations 2-21 to 2-28 in section 2.4.1.

	Elements		
	<u>Si</u>	<u>S</u>	<u>Ca</u>
Y_0	0.0161	0.0364	0.0493
Y_1	0.74	0.4266	0.16054
Y_2	$\frac{3493}{M(Si, x)}$	$\frac{1594}{M(S, x)}$	$\frac{432}{M(Ca, x)}$
U	$\frac{1.744 M(Al, x)}{M(Si, x)}$	$\frac{1.744 M(Al, x)}{M(S, x)}$	$\frac{1.744 M(Al, x)}{M(Ca, x)}$
V	$\frac{2411}{M(Si, x)}$	$\frac{2411}{M(S, x)}$	$\frac{2411}{M(Ca, x)}$

b) SILICON

	<u>S</u>	<u>Ca</u>
Y_0	0.03773	0.0511
Y_1	0.5765	0.21695
Y_2	$\frac{1950}{M(S,x)}$	$\frac{53C}{M(Ca,x)}$
U	$\frac{1.744 M(S_1,x)}{M(S,x)}$	$\frac{1.744 M(S_1,x)}{M(Ca,x)}$
V	$\frac{2422}{M(S,x)}$	$\frac{2422}{M(Ca,x)}$

c) SULFUR

	<u>Ca</u>	<u>Fe</u>
Y_0	0.0584	0.0779
Y_1	0.3763	0.1023
Y_2	$\frac{765}{M(Ca,x)}$	$\frac{167}{M(Fe,x)}$
U	$\frac{1.744 M(S,x)}{M(Ca,x)}$	$\frac{1.744 M(S,x)}{M(Fe,x)}$
V	$\frac{2452}{M(Ca,x)}$	$\frac{2452}{M(Fe,x)}$

d) CALCIUM

$$Y_0 \quad \frac{\text{Fe}}{0.09743}$$

$$Y_1 \quad 0.27192$$

$$Y_2 \quad \frac{296}{M(\text{Fe}, x)}$$

$$U \quad \frac{1.744 M(\text{Ca}, x)}{M(\text{Fe}, x)}$$

$$V \quad \frac{2903}{M(\text{Fe}, x)}$$

APPENDIX IIPROCEDURE FOR PREPARING A POLISHED SPECIMEN

The pulverized coal sample of 10 gms is dispersed in water using a combination of dispersants which have been found suitable (1) for coal and coal-mineral compositions. These are 0.3% Daxad 11 KLS (supplied by W. R. Grace and Company, Cambridge, Massachusetts), 0.2% Calgon (supplied by Calgon Corporation, Pittsburgh, Pennsylvania) and 0.1% NPS tergiton (supplied by Dow Chemical Company, Midland, Michigan) in water. The dispersed coal slurry is wet sieved through micromesh sieves (Buckbee Mears Company, St. Paul, Minnesota) to obtain closely sized fraction. The sieves with the following pore opening are used: 90 μm , 75 μm , 63 μm , 45 μm , 30 μm , 20 μm , and 10 μm . In this way a pulverized coal sample is cut into size fractions of +90 μm , 90-75 μm , 75-63 μm , 63-45 μm , 45-30 μm , 30-20 μm , 20-10 μm , and 10-0 μm . Each fraction is washed twice with distilled water and stored after drying in a vacuum oven at around 70°C for 30 minutes at 100 torr.

For making the pellet, coal is dried in a vacuum oven at 100°C and 100 torr for 1 hour. Three grams of paraplex 60 (supplied by Tenneco Chemicals, Piscataway, New Jersey) are mixed with 3 grams of epoxy resin (supplied by Folsycience Incorporated, Warrington, Pennsylvania) and 2 grams of barium

methacrylate. The mixture is heated to 80-85°C for 10 minutes. It is centrifuged to remove any undissolved barium methacrylate. Two drops of cumene hydroperoxide and one drop of cobalt activator are added to the clear mixture of resins. The two chemicals were obtained from the same company that supplied paraplex 60. Cumene hydroperoxide is a hardener while DRM cobalt is an activator. The mixture is mixed thoroughly and 1-2 gms of dried coal are added to it. The coal-resin mixture is stirred so the coal may disperse completely. It is then centrifuged for a minute and heated to 60°C for five minutes and centrifuged again. The viscous mixture is further dried in a vacuum at 50°C and 500 torr for five minutes, followed by centrifuging for two minutes.

The mixture is now allowed to harden for two hours at 45°C and 100 torr, after which the pellet is removed and washed with water and stored. The purpose of using centrifuging and vacuum drying is to avoid formation of microbubbles, or voids in the pellet. Even though a human operator can easily distinguish holes from coal grains, the voids will appear as coal grains in an automated analysis.

During centrifuging some heavier particles tend to segregate. Hence to prepare a polished surface of the pellet, a section parallel to the direction of centrifuging is chosen for polishing. The surface of the pellet is ground on a revolving wheel covered with Carborundum Company number 400 and 600 silicon carbide grit. The pellet surface is further polished on a revolving

steel wheel covered with a polishing cloth coated with hydrated alumina (0.3 μm size) and water. Final polishing is carried out using a polishing cloth impregnated with alumina (0.05 μm) set in a rotating wheel. The polished surface is cleaned for 10-15 seconds in an ultrasonic bath then washed with distilled water and air dried and stored in a dessicator.

Before actual analysis is performed, a carbon layer of 100-200 Å is deposited on the polished surface using the conventional technique of a carbon arc in a vacuum.

Reference

1. Datta, R. S., "Rheology and Stability of Mineral Suspensions", Ph.D. Thesis, The Pennsylvania State University, 1977.

APPENDIX III

PROCEDURE FOR PRODUCING A DISPERSED SPECIMEN

About 30-35 mgm of pulverized coal sample are dispersed in 3-4 ml of a mixture of surface active agents, to give a dispersing solution of 0.2% NPX Tergiton, 0.1% calgon and 0.1% Daxad 11 KLS. The suppliers of these chemicals have been mentioned in Appendix II. The mixture was applied in the sequence: coal + calgon solution is stored, NPX-Tergiton added, shaken and Daxad added finally. The suspension is then treated for one minute in an ultra-sonic bath prior to preparing the slide. Calgon is a dispersing agent for minerals, NPX-Terigiton is a wetting agent for coal and Daxad is a dispersant for coal.

With the help of a pipette a drop (approximately 0.1 gm) of the dispersed sample is transferred to a cleaned carbon planchet surface. The drop is covered with a slide cover and the slide is cooled (by liquid nitrogen) to freeze the sample. The glass slide cover is twisted off using a razor blade, leaving a frozen thin layer of the sample on the carbon planchet. The carbon planchet is then put in a vacuum system, where the ice is sublimed off without melting the sample. After the ice has sublimated, the slide is viewed under a microscope to check the absence of agglomerates. If agglomerates are present, a fresh slide is prepared.

Before analyzing the slide, carbon is deposited on it using a carbon arc in a vacuum.

APPENDIX IV

TYPICAL MINERALS IN COAL (1,2)

Mineral	Formula	Usual proportions in coal
Shale group	$(K, Na, H_3O_3, Ca)_2 (Al, Mg, Fe, Ti)_4 (Al, Si)_8 O_{20} (OH, F)_4$	
Clay group (kaolinite)	$Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$ $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	Usually amounts to 50-90% of mineral matter
Sulfur group	$FeS_2, FeSO_4, Na_2SO_4$	Iron in any proportion from 0 to 20% sodium and potassium from 0 to 4% sulphur from 0.5 to 10%
Carbonate group	$CaCO_3, CaCO_3, MgCO_3$	Calcium from 0 to 20%, magnesium from 0 to 8%
Associated minerals		
Quartz	SiO_2	The balance generally contains the following elements: Sodium, potassium 0-4% Titanium 0-2% Magnese Small proportions P, Ni, B, Zr, P Occasionally found in small quantities (<1%)
Feldspar	$(K, Na)_2O \cdot Al_2O_3 \cdot 6SiO_2$	
Garnet	$3CaO \cdot Al_2O_3 \cdot 3SiO_2$	
Hornblende	$CaO \cdot 3FeO \cdot 3SiO_2$	
Gypsum	$CaSO_4 \cdot 2H_2O$	
Apatite	$9CaO \cdot 3P_2O_5 \cdot CaF_2$	
Epidote	$4CaO \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot H_2O$	
Biotite	$K_2O \cdot MgO \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$	
Augite	$CaO \cdot MgO \cdot 2SiO_2$	
Magnetite	Fe_3O_4	
Kyanite	$Al_2O_3 \cdot SiO_2$	
Hematite	Fe_2O_3	

References

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- Nelson, H. W. et al., "A Review of Available Information on Corrosion and Deposits in Coal and Oil-Fired Boilers and Gas Turbines", ASME, New York, pp. 7-12, 1959.

APPENDIX V**MINERAL TRANSFORMATIONS DUE TO HEATING (1)**

Reference

1. Gluskoter, H. J. and Mitchell, R. S., "Mineralogy of Ash of Some American Coals: Variation with Temperature Source", Fuel, 55, 2, 1976.

APPENDIX VI

PRINCIPAL REACTIONS UNDERGONE BY
MINERAL MATTER DURING COMBUSTION (3)

Species	Reaction	Approx. reaction (temp. °C)	Remarks
Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$ $\downarrow$ $\text{Al}_2\text{O}_3 + 2\text{SiO}_2$	550-600	On rapid heating, H_2O may be retained to 1000°-1200°C.
Pyrite FeS_2	$2\text{FeS}_2 + \frac{11}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_2$ $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$ $\text{FeS}_2(\text{s}) \rightarrow \text{FeS}_2(\text{g})$	500 MPt-1195(FeS) MPt-1172(FeS ₂)	On slow heating. On faster heating or in reducing conditions. On very rapid heating (Reid (1)) (Hein (2)) argues that sulphides evolved under reduction conditions result in deposition using German brown coals.
Sulphates CaSO_4 MgSO_4 $\text{Fe}_2(\text{SO}_4)_3$ Na_2SO_4	$\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$ $\text{MgSO}_4 \rightarrow \text{MgO} + \text{SO}_3$ $\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_3$ $\text{Na}_2\text{SO}_4(\text{l}) \rightarrow \text{Na}_2\text{SO}_4(\text{g})$	1180 d.1124 d.480 MPt-884	MPt-1450, decomposition calculated by Padia (3) Exists as vapor above MPt. Vapor is not saturated even for high Na coals. Decomposition to Na_2O is not favored.
Carbonates CaCO_3 $\text{CaMg}(\text{CO}_3)_2$	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2$	710-950 740-800	
Chlorides NaCl KCl	$\text{NaCl}(\text{l}) \rightarrow \text{NaCl}(\text{g})$	MPt-800, BPt-1465	On rapid heating (p.f.), the vapor is evolved. For most coals the vapor pressure is below saturation. Reaction with SiO_2 to give silicates may reduce vapor pressure. (Boow (4)).
$3\text{NaCl} + (\text{Na}, \text{K})\text{aluminosilicate} \rightarrow (\text{Na})\text{aluminosilicate} + \text{KCl}(\text{g})$ $\text{NaCl} + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_2 + 2\text{HCl}$			Reask (5) On slower heating. Reaction rate may limit.

References

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2. Hein, K., "Research into the Combustion and Fouling Behavior of German Brown Coals", in International Conference on Ash Deposits and Corrosion from Impurities in Combustion Gases, New England College (ASME Research Committee), June 26-July 1, 1977.
3. Padia, S. P., Sarofin, A. F., Howard, J. B., "The Behavior of Ash in Pulverized Coal Under Simulated Combustion Conditions", paper presented at Combustion Institute's Central State Section Spring Meeting, 5-6 April, 1977. Also D.Sc. Thesis with same title by S. P. Radia, Department of Chemical Engineering, Massachusetts Institute of Technology.
4. Boow, J., "Sodium Ash Reactions in the Formation of Fireside Deposits in Pulverized-Fuel-Fired Boilers", Fuel, 51, 170, 1972.
5. Raask, E., "Cenospheres in Pulverized Fuel Ash", J. Inst. of Fuel, 41, 339-344, 1948.

APPENDIX VII

SLAGGING AND FOULING PARAMETERS (1)

APPENDIX VII

SLAGGING AND FOULING PARAMETERS (1)

1. Total acids in a coal ash is the sum of the percentages of SiO_2 , TiO_2 and Al_2O_3 in the ash. In pyrochemical terms an acid is a metal oxide when molten will flux basic oxide.
2. Total bases in a coal ash is the sum of the percentage of Fe_2O_3 , CaO , MgO , K_2O and Na_2O in the ash. In pyrochemical terms base is a metal oxide which is readily dissolved or fluxed by an acid.

Acids generally tend to have smaller cationic radii and larger ionic potential (2) as compared to bases.

3. Base to acid ratio related to ash melting and viscosity is the ratio of total base to total acid. At values less than 0.75, the melting temperature and viscosity of the ash at any given temperature decrease as base to acid ratio increases.
4. Slagging factor is computed as:

$$\text{Slagging factor} = (\text{Base/Acid}) \times \% \text{ S in dry coal}$$

This factor is claimed by its developers that it gives a reasonable correlation with slagging problem, particularly for dry bottom furnaces.

5. Fouling factor is computed as:

$$\text{Fouling factor} = (\text{Base/Acid}) \times \% \text{ of } \text{Na}_2\text{O} \text{ in ASTM ash.}$$

This factor is claimed to be useful in predicting fouling problems of convection section surfaces.

Both slagging and fouling factors are to be used for certain types of ashes only. This distinction is based on relative ratio of Fe_2O_3 to $\text{CaO} + \text{MgO}$.

6. Dolomite percentage is expressed mathematically as

$$\text{Dolomite percentage} = \frac{\% \text{CaO} + \% \text{MgO}}{\% \text{Fe}_2\text{O}_3 + \% \text{CaO} + \% \text{MgO} + \% \text{Na}_2\text{O} + \% \text{K}_2\text{O}}$$

Dolomite percentage is related to viscosity and fusion temperature. At a given percent base, higher dolomite percentage indicates higher melting point and higher viscosity ash.

References

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