A STUDY OF FLY ASH REACTIONS AND DEPOSIT FORMATION IN A LARGE, CYCLONE-FIRED STEAM GENERATOR

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Introduction

Many, if not most, of the problems peculiar to the use of coal as a fuel are related to its mineral matter content. The ash and slag products cause fouling and sometimes corrosion of heat transfer surfaces, are hard to remove when slag deposits become massive, are difficult to contain when the slag is fluid, and are costly to remove as particulate matter in the stack gases. The purpose of this paper is to discuss the release of mineral matter in burning coal and to present data on reactions of ash deposits with combustion product gases in a large cyclone-fired steam generator. Conclusions will be drawn that must be interpreted as pertinent to the particular unit though based in part on observations in other units. The intent is to demonstrate that valuable information can be gained by systematic sampling and analysis of fly ash and ash deposits.

The Release of Mineral Matter

Ash, as formed from the mineral matter of coal in the ASTM Standard Method,[1/] has analyses as illustrated by samples 8 and 9 of Table I for two Illinois coals. Several things are noteworthy: 1) Carbonates are converted to oxides, 2) sulfur is retained as sulfate to the extent that sulfate formation precedes carbonate decomposition, and 3) the weight percentages of ash components, represented as oxides, add approximately to 100%. When the ash is formed under high-temperature conditions, as in the steam generator furnace rather than the temperature-controlled muffle furnace used for the ash determination, a lesser proportion of the sulfur is retained as sulfates and the alkali metals are at least partially volatilized. Vapor pressures for various alkali materials are given in Table II. The free alkali metals are most volatile, but equilibria favor conversion to the hydroxides. The oxides should be considered, although equilibria also favor their conversion to the hydroxides. Little information is available on the kinetics of such high-temperature, gas-phase reactions. Acid-base reactions are fast in water solution but may be slow in the gas phase. HCl gas seems relatively inert. Alkaline mists have been observed to fall out of the plume from incineration of organic wastes with high NaCl content. These considerations suggest that the hydroxides are the probable mode of transport of alkali metals in the hot combustion gases.

TABLE I.- Analyses of ash and slag samples, weight percent

No.	Location	SO_3	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	Na_2O	K_2O	Total
1	Slag tank	0.25	19.7	17.6	45.8	8.67	0.95	2.16	1.99	97.1
3	Reheat superheater	10.2	21.0	16.4	32.5	10.95	.80	2.80	2.19	96.8
4	Primary superheater	2.2	18.6	18.3	47.1	5.96	.86	2.47	2.04	97.5
5	Economizer hopper	5.0	20.6	17.4	43.2	5.79	.75	2.56	2.13	97.4
6	Air heater hopper	2.2	21.7	17.6	45.4	7.61	.86	2.12	2.05	99.5
7	Precipitator hopper	3.5	18.9	17.6	45.8	5.04	.90	2.91	2.82	97.5
8	Coal ash, A	7.5	28.2	15.5	35.7	7.68	.78	2.43	1.83	99.6
9	Coal ash, B	8.0	17.2	18.9	44.5	7.55	.91	1.98	1.83	100.9

TABLE II. - Temperatures at selected vapor pressures

Component	T °C 1 mm	10 mm	100 mm
Na	439	549	701
K	341	443	586
NaOH	739	897	1111
KOH	719	863	1064
NaCl	865	1017	1220
KCl	821	968	1164

Iron sulfide, FeS, and metallic iron tend to appear with deficient air supply. This is aggravated in wet bottom furnaces when pyrite (FeS_2) impinges on the slag surface. The iron in coal is present primarily as pyrite. Bailey and Ely[2] have shown that iron tends to segregate into slag and into furnace deposits. The author has observed a furnace with front wall burners and a plan area too small to prevent flame impingement on the wall surfaces. Iron content of the wall slag was over three times that expected from the coal ash analysis. It appeared that oxygen was deficient in the area of flame impingement and that liquid droplets of FeS were preferentially adhering to the wall, although intermittent oxidation gave an oxidized slag.

Fireside corrosion associated with segregated deposits high in alkali-iron sulfates were first found on furnace wall tubes of wet bottom furnaces.[3,4] Presence of CO in the local gas stream was indicative of local oxygen deficiency and flame impingement with preferential adherence of FeS droplets and high local heat transfer rates. However, the segregated deposits were found to be sulfates with detectable sulfide only at the interface between the deposit and the tube metal. Intermittent oxidizing conditions convert sulfides to sulfates. With tube surface temperatures on the order of 400 °C, the complex alkali-iron pyrosulfates become stable liquids. While these liquids in part may be corrosion products, they in turn are cause for electrolytic corrosion if not the active corrosive agents.

Reactions between sulfur oxides and fly ash have been the subject of study and speculation for many years. Johnstone[5] concluded that fly ash from stoker-fired boilers had a little catalytic action on the oxidation of sulfur dioxide in flue gas. Crossley, Poll and Sweett[6] studied these reactions to explain findings of the Boiler Availability Committee that firing of pulverized coal over the back end of mechanical stokers was effective in controlling acidic deposits in the boiler. The appearance of the typical alkali-iron-aluminum sulfates on superheater tubes brought renewed interest in the reactions between fly ash and combustion gases. The extensive literature has been reviewed by Reid.[7] The deposits are characterized by water solubility, a low pH, high content of alkali, iron, aluminum and sulfate, and relatively low contamination by other constituents of fly ash. These deposits underlie typical ash deposits. They have an amorphous or microcrystalline appearance when cold but sometimes show signs of having been liquid. They appear where gas temperatures, the thickness of the overlying ash deposit, and the steam conditions are such that the resulting heat transfer produces temperatures near the tube surface approaching 650 °C. The segregated deposit may be separated from the tube metal by a poorly consolidated oxide scale. The author has also found samples where liquid wetted the metal tube and penetrated under the oxide scale so as to bend it away from the tube surface. Relatively low occlusion of fly ash in the segregated deposit indicates that components not soluble in the deposit are mechanically ejected by cyclic melting and solidification. The resulting deposit, from American bituminous coals, has a somewhat variable composition, particularly the

proportion of iron and aluminum sulfates, but is so characteristically different from the overlying fly ash deposits that it is visually detectable without need for chemical analysis.

Occurrence of the segregated deposit under typical ash deposits has caused speculation as to whether the deposit was formed first and the fly ash deposited later or whether the segregated material was synthesized beneath the fly ash deposit.

Synthesis of the complex sulfates requires a partial pressure of SO_3 higher than that found in the main stream of combustion gases. Anderson and Goddard[8] conclude that the SO_2-SO_3 reaction reaches equilibrium within the deposit and that solution phenomena at operating temperatures reduce the necessary partial pressure of SO_3 below that exhibited by pure phases of alkali-iron and alkali-aluminum sulfates that appear in the deposit after cooling.

While information on reactions between sulfur oxides and fly ash is sketchy, there is even less information on reactions involving the alkali metals. Weintraub, Goldberg and Orning[9] found that the alkali content of fly ash, subjected to a temperature gradient in a flue gas atmosphere, migrated towards a cold surface at 375°C. The complex alkali sulfates did not appear. In the absence of a supply, beyond that of the original fly ash, there was insufficient alkali for the synthesis. Since the alkali components of the mineral matter of coal are volatile under combustion conditions, it seemed desirable to gather data on the reabsorption of alkali by fly ash and by deposits at various points within a coal-fired steam generator. A study of deposits in a cyclone-fired unit seemed preferable because the high temperatures within the cyclone would assure more complete volatilization of the alkali components.

The Steam Generator

The steam generator cross section is shown in Fig. 1. It was rated at 3,290,000 lb of steam/hr, 3625 psig and 1005°F superheat with 575 psig and 1005°F reheat. It had 10 cyclones, 10 ft in diameter, five each on the front and rear walls. Sampling points are shown by the circled numerals, except for the electrostatic precipitator hopper which is not shown. The furnace wall tubes were fully studded to a level about 5 ft below the gas recirculation ports. A thin, glassy slag coat was intact throughout the studded zone following shutdown. Slag shedding had occurred on all upper wall surfaces except in the corners just above the studding and on the walls under some of the gas recirculation ports.

Ash and Slag Samples

Two southern Illinois bituminous coals were used. Analyses of the ash and slag samples are shown in Table I. Data on the mole percent basis, shown in Table III, are more revealing. Unfortunately, the two coals that were used have somewhat different ash analyses. The SO_3 is equivalent to about 70% of the CaO for both coal ashes, while sulfur in ash accounted for 24.6% of the sulfur in coal A and 38.5% of the sulfur in coal B. Retention of sulfur in the coal ash, as produced at 700° to 750°C by the standard method for ash content, is related to the calcite content rather than to the sulfur content of the coal.

The composition of various slag, deposit, and fly-ash samples may be expected to depend upon opportunities for segregation, on temperatures at various points along the gas flow path, and on the readsorption of sulfur and alkali components. The temperatures were not measured but were probably on the order of over 1700°C in the cyclone, 1000°C in the secondary superheater, location 2, and 325°C at the air heater, location 6.

TABLE III.- Ash analyses, mole percent, and physical characteristics

No.	Location	Color[a]	Mag.[b]	SO_3	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	Na_2O	K_2O
1	Slag tank	BL.	1	0.2	9.5	13.3	59.0	11.9	1.8	2.7	1.6
6	Air heater	BL.	3	2.1	10.4	13.2	58.0	10.4	1.6	2.6	1.7
4	Primary superheater	R.B.	2	2.2	8.9	13.9	60.4	8.2	1.6	3.1	1.7
5	Economizer hopper	B.R.	2	4.9	10.2	13.4	56.7	8.2	1.5	3.3	1.8
3	Reheat superheater	B.R.	0	10.2	10.5	12.9	43.6	15.7	1.6	3.6	1.9
7	Precipitator hopper	G.B.	2	3.4	9.2	13.4	59.4	7.0	1.7	3.6	2.3
8	Coal ash, A	-	-	7.6	14.3	12.3	48.3	11.1	1.6	3.2	1.6
9	Coal ash, B	-	-	7.5	8.0	13.8	55.2	10.0	1.7	2.4	1.4

[a]Color code: BL., black; R.B., red-brown; G.B., gray-brown; B.R., brick-red.
[b]Scale of increasing magnetic character.

Sulfur content of the slag is almost immeasurably low. The 0.2 mole of SO_3 corresponds to 0.1 wt percent of sulfur, which is reported to the nearest 0.1%. The sodium and potassium contents of the slag are comparable to those of the coal ashes. Slag from the cyclones flows across the furnace floor to the slag drip. Either the alkali metals were not substantially volatilized in the cyclones or they were readsorbed as the slag flowed across the furnace floor.

Deposit samples were not taken from location 2, Fig. 1 (lead tube of the last platen of the secondary superheater). Visually identifiable complex alkali-iron-aluminum sulfate, covered by a thin shell of ash, was found on these tubes. The ash shell had partially shed on cooling of the furnace. Large sections could be removed intact with light finger pressure on the edge to expose the underlying sulfate deposit. The shell was so thin that clean separation from the underlying sulfate deposit could not be assured for the purpose of chemical analysis.

Deposits at location 3 (lead tube of the reheat superheater platen) were shaped like antlers jutting into the gas stream and were joined by a thin shell across the front of the tube. They were so hard that the author could not break them off by hand though they projected about 3 inches in front of the tube. The analysis gave an exceptionally high content of SO_3 and maximum values for the alkali metals, except K_2O in the precipitator hopper sample. The surface of the deposit was dusty, and fracture surfaces showed no indication of fusion, suggesting that the ash was cemented by formation of alkali sulfates within pores of the deposit.

The samples from location 4 (the top of the primary superheater) were hard nodules blown from an unknown location and too large to pass between the superheater tubes. While these nodules were as hard as sample No. 3, the sulfur content was not as high. The underlying tubes were free of deposits.

The economizer hopper (location 5) was located below the downflow section of convective heat transfer tubes. The air heater hopper was under the flow reversal duct between sections of the air heater. The classifying action of changes in flow direction, compared to electrostatic precipitation, may be responsible for the differences in analysis between samples from the economizer hopper, the air heater hopper, and the precipitator hopper, locations 5, 6, and 7. There is also a progressive drop in temperature between these locations.

The sample analyses are remarkably consistent except for the variation in SO_3 content and a disproportionation between lime and silica in sample No. 3. The iron content of the hopper and deposit samples is between those of the two coal ashes, while the silica contents, with the one exception, are higher than that of either coal ash.

The hopper and deposit samples showed remarkable differences in color and magnetic properties. Table III gives data from gross appearance. Microscopic examination showed heterogeneous character. The slag tank sample looked like pulverized black glass with a few translucent wedges and a few magnetic particles, presumably magnetite. The brick-red material from the reheat superheater tube had a very small number of magnetite particles. The economizer hopper and superheater nodule samples had increasing proportions of magnetite mixed with the brick red. The air heater sample appeared almost as black as the slag tap sample, and had a large portion of magnetite with a sprinkling of small red particles on the surface of the larger black particles. The precipitator hopper sample had a considerable portion of magnetite with enough whites (some opalescent beads) and reds to give a gray-brown appearance. Almost all black particles, except those from the slag tank, were magnetic, presumably magnetite. The analyses for iron are given in terms of Fe_2O_3 without regard to the actual state of oxidation. The brick red color is due to ferric oxide, and the color variations may be used to infer variations in ferric oxide content.

Discussion

Most of the ash from cyclone combustion is collected in the slag tank with almost negligible sulfur content. Deposits with high sulfur content are formed over long periods of time and represent a negligible part of the material balance. The fly ash has a significant sulfur content but represents a minor fraction of the mineral matter input. Most of the sulfur passes through the system as SO_2, but oxidation to SO_3 and sulfate formation by reaction with other mineral matter components have considerable effect on deposit formation.

The behavior of iron is of particular interest. It is present in the coal almost entirely as pyrite, often distributed as very fine particles. Rapid heating to 2200°C produces liquid droplets approximating FeS, ferrous sulfide.[10] The sequence of melting, decomposition, and oxidation is unknown. Larger particles are probably thrown onto the slag within the cyclone. Smaller particles are converted in suspension to finely divided ferric oxide. The author has observed a cyclone-fired unit with a mechanical but no electrostatic precipitator. The stack plume was brick red. Had it been black it would have been rated number 4 smoke. The finely divided ferric oxide produces a dust coating on tube surfaces. At appropriate temperature levels, oxidation of SO_2 to SO_3 within the dust layer and reaction with adsorbed alkali metals produces the complex alkali-iron sulfates. Depending upon temperatures and temperature gradients, these sulfates may act as cementing agents or may accumulate as a segregated phase near the tube surface. Cyclic melting and freezing then causes ejection of non-soluble particulates and accumulation of the segregated deposit.

A systematic variation in alkali metal content was not apparent until the data were arranged in the sequence of Table III. Data for the slag tank sample are listed first. Those for the precipitator hopper sample and the coal ashes are listed last. Intervening data are in the sequence of increasing content of ferric iron as inferred from color. Variation from the sequence of positions along the flow path is a result of segregation of particulate matter and the action of retractable blowers used periodically to blow loose deposits off tube surfaces. The highest content of ferric iron was found in the hard deposit on the reheat superheater tube. Dusty deposits are blown off the tubes by the retractable blowers.

Depending upon agglomeration, these tend to fall out in the economizer hopper or carry through to the electrostatic precipitator. Absorption of the alkali metals appears to be favored by the finely divided ferric oxide with some effect of temperature on opportunities for sulfate formation. Temperatures are lowest in the precipitator. Conditions are most favorable for reaction with SO_3 within deposits on the secondary superheater, location 2, and the reheat superheater, location 3. Material balances are obscured by differences between the coals and the unknown times required for deposit formation. High SO_3 content in segregated deposits is negligible in comparison to total flow over the time of their formation. Relatively high content in the precipitator sample is offset by the larger portion of the total ash collected in the slag tank. Immeasurably lower content in the slag tank sample is sufficient to provide material balance. The disproportionation of MgO and SiO_2, in the deposit at location No. 3, the reheat superheater lead tube, is explainable in terms of the results of intermittent operation of retractable blowers. Acid formation and alkali adsorption extend through the interface between the cemented deposit and the dusty outer coat. Basic constituents, as against the acidic silica present in segregated particles, are preferentially retained when the dust coating is intermittently removed by the blower action.

Recommendations for Future Study

Data presented here are for samples taken from a cyclone-combustion-fired unit. It has often been observed that these units produce reddish fly ash rather than the typical gray fly ash from pulverized-coal-fired systems, indicating the presence of finely divided ferric oxide. Nevertheless, the data indicate the possibilities for better understanding of the reactions involved in deposit formation. Supplemental data on temperatures, gas compositions, and particulate samples taken from the gas stream at various points along the gas flow path would be helpful. Preparation for taking samples from less accessible positions would also be helpful.

Laboratory studies of reactions between gases and mineral matter components become meaningful only when interpreted in relation to the conditions and materials that exist within actual steam generator systems. Laboratory studies should be encouraged, but they must be coordinated with actual conditions in large steam generators.

Conclusions

1) Samples of fly ash and deposits were obtained from various locations in a large, cyclone-fired steam generator.

2) Wide variations in color were due to variations in ferric oxide content.

3) Variations in alkali metal content were related qualitatively to variations in ferric oxide content and temperatures.

4) Typical segregated deposits of complex alkali-iron-alumina sulfates were visually identified within the secondary superheater.

5) A hard deposit on the reheater superheater probably was formed by the cementing action of sulfates formed within the pores of an overlying dusty deposit and incremental buildup of cemented material left after each cycle of retractable blower operation.

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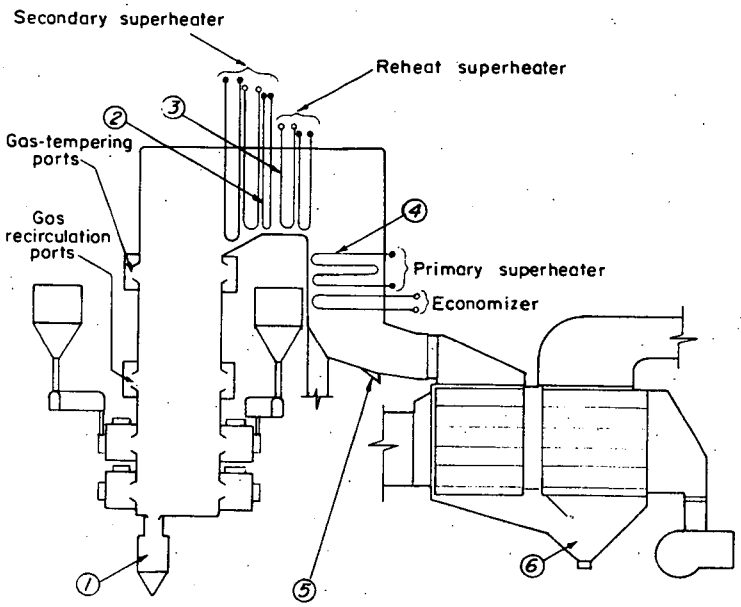

Figure 1.- Sampling locations in the cyclone fired steam generator. Location 7, the precipitator hopper is not shown.