

A STUDY OF SLAG DEPOSIT INITIATION IN A DROP-TUBE TYPE FURNACE

Murray F. Abbott* & Leonard G. Austin

Fuel Science Section and Department of Mineral Engineering
The Pennsylvania State University
University Park, PA 16802

ABSTRACT

A drop-tube furnace was designed and constructed for the purpose of simulating the time/temperature environment for p.c. combustion in a utility furnace. The ash produced was impacted on oxidized boiler steel coupons at gas and metal temperatures similar to upper furnace waterwall tubes. Both fly ash and deposits were similar to those of a pilot-scale (7-9 kg/hr) combustor. Iron-rich slag droplets produced from pyrite-rich p.c. particles bonded strongly with the oxidized steel surface. These particle types were found at the base of ash deposits after removal of sintered and loose ash for both eastern and western coals. Adhesion of iron-rich droplets was a function of both flame and metal surface temperatures. Also, volatile species, i.e., alkali and exchangeable cations influenced the "sticking" behavior of the iron-rich droplets. These trends are in qualitative agreement with previous sticking test results.

INTRODUCTION

All coals contain inorganic matter which is converted to ash when the coal is burned. The management of this ash constitutes one of the principal limiting design considerations for a p.c. steam generator. Operational problems occur if ash deposition and build-up on heat exchange surfaces becomes unmanageable. A single day's outage for an 800 MW unit for ash removal and repair can cost the utility as much as \$600,000 in lost electrical generation (1). Derating of the boiler system to manage ash deposition problems can cost millions of dollars annually. This investigation is part of an ongoing research program to gain a better fundamental understanding of the initiation of slag deposits on the upper walls of a boiler furnace enclosure. This paper reports on the development of a gas-fired vertical muffle tube (drop-tube) furnace as a new research tool.

A previous laboratory test, the sticking test (2-7) led to a number of conclusions concerning the mechanism and chemistry of molten slag drop adhesion to oxidized boiler steels. However, this test had several inherent disadvantages. It required the use of comparatively large molten ash drops (2 mm in diameter) and there was no proof that the conclusions applied equally well to the smaller size droplets (submicron to 250 μ m) produced in p.c.-fired furnaces. Also, the large drops formed from a coal ash contained all of the constituents of the ash (mean ash composition) which cannot accurately simulate the variety of mineral associations occurring on a particle-by-particle basis in a pulverized coal (8). Thus, the purpose of the drop-tube furnace was to produce coal fly ash particles under the same time/temperature environment experienced in full-scale boiler combustion followed by impaction on an oxidized boiler steel coupon simulating an upper furnace waterwall surface.

EXPERIMENTAL

Three Pennsylvania bituminous coals, designated Keystone, Montour and Tunnelton and a Decker, Montana subbituminous coal were studied in this investigation. All are current steam coals. Semi-quantitative mineralogical analysis of LTA and spectrochemical analysis of ASTM HTA are given in Table 1 for the three

*Current Address: Babcock & Wilcox R&D, 1562 Beeson Street, Alliance, OH 44601

Pennsylvania coals and raw (untreated) and acid washed Decker coal samples.

The drop-tube furnace system in which the test coals were burned is shown in Figure 1. It consisted of four major component parts: (i) a gas-fired hot zone, (ii) a fluid-bed feeding system, (iii) a preheat section and injector, and (iv) a water-cooled ash collector probe. The conditions inside the heated muffle tube simulated those of a utility furnace combustion zone: (i) maximum gas temperatures of 1500 to 1750°C, (ii) particle residence times between one and two seconds, and (iii) ash sampling temperatures ranging from 1000 to 1300°C. The fluid-bed feeder delivered between 0.2 and 0.3 grams of pulverized coal with slightly less than 1 liter of primary air per minute. In the preheat section the secondary air stream (roughly 2 liters/min) was heated to about 1000°C before a honeycomb flow straightener distributed it in streamlines across the muffle tube cross-section. The cold p.c./primary air mixture was carried by the injector to the hot combustion zone. A thin pencil-like p.c. stream was burned as it passed through the heated muffle tube. The fly ash produced was accelerated and impacted onto a water-cooled boiler steel coupon at surface temperatures of 300 to 450°C.

The ash deposits were characterized physically by observation under both a Zeiss optical and IDS-130 scanning electron microscope (SEM). Chemical characteristics were determined by energy dispersive x-ray fluorescence equipment associated with the SEM.

RESULTS AND DISCUSSION

Physical characteristics for all ash deposits were similar. Figure 2 shows a typical ash deposit structure on both a macro and microscale. The top photograph (A) shows an ash deposit collected from the raw Decker coal on a Croloy 1/2 steel coupon. The lower optical photomicrograph shows the strongly bonded material remaining on the surface after the comparatively loosely adhered ash had been brushed away. The opaque black droplets are rich in iron (85 to 100 wt. %) and the light colored transparent glassy spheres are predominantly aluminosilicates. The deposit build-up mechanism appeared to be similar for all coals. All originated with the relatively strong bonding of iron-rich slag drops to the oxidized steel surface. Aluminosilicates were only found in this layer for the raw Decker coal. In addition, there was always a layer of very fine particles (submicron) covering the entire coupon surface. It was not possible to brush or blow this layer from the surface. A region of loosely bonded ash particles often containing most all of the major constituents of the ash then built upon the more strongly adhered droplets. There was little if any interaction between the loose ash and adhesive particles. As the distance from the steel surface increased the ash particles began to sinter, eventually forming a fluid mass in some instances.

Preferential deposition of iron-rich species has been suggested by other investigators (9,10). It was also observed in a pilot-scale p.c. test combustor (11). The fine particle layer probably formed on the coupon surface due to convective diffusion to the relatively cold steel coupon (12). Presumably the scouring action of the ash laden gases in a utility furnace would prevent formation of the loose ash layer until the iron-rich layer is more extensively developed and interaction with successive layers can occur.

The iron-rich deposit base particles formed from the Keystone coal at flame temperatures of 1470 (A) and 1500°C (B) are shown in the SEM photomicrographs in Figure 3. The concentration of these particles increased with increasing flame temperature. Note that the particles flattened more on impact at the higher temperature, probably due to a decrease in particle viscosity. There appeared to be two different iron-rich particle types in each deposit: (i) a porous particle with a rougher surface texture, and (ii) a more glassy appearing particle with a very smooth surface texture. X-ray fluorescence spectrograms are also shown in Figure 3. The porous type particles were found to contain exclusively iron (see analysis of Point 1 in Figure 3B), whereas the more glassy particle types contained smaller amounts of silicon, aluminum and potassium (Point 2).

The two furnace operating parameters which most influenced ash deposition rates

were flame and coupon surface temperatures. Both of these trends are shown in Tables 2 and 3. Deposit build-up rates increased between two and six times with each increase in flame temperature and ten-fold for a 30 degree rise in coupon surface temperature. Removing exchangeable cations from the Decker coal caused a three-fold decrease in the ash deposition rate, see Table 4. The exchangeable cations appeared to play a significant role in both the initial iron-rich deposit and the sintering properties exhibited by the ash deposit. The sintered ash collected from the raw Decker coal was yellow-brown in color and comparatively difficult to break apart requiring a force of nearly 20 psi. The acid form sinter was coral colored and broke apart while removing the coupon from the collector probe.

CONCLUSIONS AND FUTURE WORK

The drop-tube furnace closely simulated the time/temperature history of a utility boiler furnace. One type of slag deposit initiating particle which strongly bonds to oxidized boiler steels is low melting iron-rich droplets produced from pyrite-rich p.c. particles. Flame and metal surface temperatures strongly influence ash deposit build-up rates. Sufficient evidence exists to suggest that alkalis and calcium enhance the "sticking" behavior of iron-rich and other fly ash droplets. This investigation revealed a qualitative relationship between results obtained from several different apparatus used to study slag initiation: (i) sticking apparatus, (ii) drop-tube furnace, and (iii) pilot-scale p.c. test combustor.

Future work in the drop-tube furnace will include: (i) developing a method for defining the relative adhesion properties of ash particle types, and (ii) more clearly defining the role of volatile species in deposit initiation and growth. This second goal can be accomplished by investigating controlled composition synthetic polymer/mineral combinations.

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TABLE 1. MINERALOGICAL AND ELEMENTAL ASH COMPOSITION FOR TEST COALS

| <u>Procedure/Coals</u> | <u>Montour</u> | <u>Keystone</u> | <u>Tunnelton</u> | <u>Raw Decker</u> | <u>Acid-Washed Decker</u> |
|--------------------------------|----------------|-----------------|------------------|-------------------|---------------------------|
| Mineralogical (wt. % LTA) | | | | | |
| Quartz | 25 | 25 | 22 | 20 | 30 |
| Pyrite | 15 | 10 | 15 | 5 | 10 |
| Calcite | 5 | -- | 5 | 5 | -- |
| Gypsum | -- | 5 | -- | 30 | -- |
| Kaolinite | 17 | 30 | 18 | 11 | 16 |
| Illite | 30 | 20 | 30-40 | -- | -- |
| Feldspan | -- | -- | 5-10 | -- | -- |
| LTA (wt. % as received coal) | 18.0 | 21.6 | 22.9 | 6.3 | 3.3 |
| HTA (wt. % as received coal) | 15.8 | 18.0 | 20.1 | 4.0 | 2.2 |
| Spectrochemical (wt. % HTA) | | | | | |
| SiO ₂ | 51.7 | 54.1 | 50.3 | 26.5 | 53.0 |
| Al ₂ O ₃ | 25.6 | 25.9 | 26.8 | 15.5 | 28.5 |
| TiO ₂ | 1.3 | 1.3 | 1.3 | 0.9 | 2.7 |
| Fe ₂ O ₃ | 14.1 | 9.7 | 11.0 | 5.3 | 9.2 |
| CaO | 2.4 | 1.8 | 2.5 | 14.3 | 4.1 |
| MgO | 0.9 | 1.0 | 1.0 | 2.5 | 0.7 |
| Na ₂ O | 0.2 | 0.3 | 0.4 | 0.03 | 0.01 |
| K ₂ O | 2.4 | 2.9 | 2.9 | 5.0 | 0.4 |
| SO ₃ | 1.5 | 1.1 | 2.3 | 0.97 | 0.6 |
| P ₂ O ₅ | 0.4 | 0.4 | 0.4 | 21.6 | -- |

TABLE 2. DEPOSIT BUILD-UP RATES FOR THE THREE PENNSYLVANIA STEAM COALS AT THREE FLAME TEMPERATURES

| Coal | Flame Temperature °C | Deposit Mass mg | Relative Build-up Rates | | Percent of Total Ash (Based on HTA) |
|-----------|----------------------|-----------------|-------------------------|------------|-------------------------------------|
| | | | mg/min | mg/gr Coal | |
| Montour | 1465 | 26.5 | 2.2 | 11.0 | 6.9 |
| | 1518 | 64.5 | 5.4 | 22.5 | 14.2 |
| | 1561 | 133.0 | 11.1 | 46.3 | 29.2 |
| Keystone | 1470 | 24.0 | 2.0 | 7.1 | 3.9 |
| | 1500 | 117.7 | 9.8 | 40.8 | 22.7 |
| | 1560 | 286.1 | 23.8 | 99.2 | 47.3 |
| Tunnelton | 1467 | 39.7 | 3.3 | 11.8 | 3.1 |
| | 1510 | 252.6 | 21.1 | 75.4 | 19.7 |
| | 1518 | 297.1 | 24.8 | 103.3 | 51.3 |

TABLE 3. DEPOSIT BUILD-UP RATES FOR THE KEYSTONE COAL AT A FLAME TEMPERATURE OF 1500°C AND TWO DIFFERENT COUPON SURFACE TEMPERATURES

| Coupon Surface Temperature °C | Deposit Mass mg | Relative Build-up Rates | | Percent of Total Ash (Based on HTA) |
|-------------------------------|-----------------|-------------------------|------------|-------------------------------------|
| | | mg/min | mg/gr Coal | |
| 310-318 | 11.7 | 6.98 | 29.1 | 2.3 |
| 340-345 | 117.7 | 9.8 | 40.8 | 18.0 |

TABLE 4. DEPOSIT BUILD-UP RATES FOR RAW AND ACID WASHED DECKER COAL SAMPLES AT A FLAME TEMPERATURE OF 1500°C

| Coal Sample | Deposit Mass mg | Relative Build-up Rates | | Percent of Total Ash (Based on HTA) |
|--------------------|-----------------|-------------------------|------------|-------------------------------------|
| | | mg/min | mg/gr Coal | |
| Raw Decker | 82 | 4.1 | 14.6 | 36.6 |
| Acid Washed Decker | 25 | 1.3 | 5.4 | 23.7 |

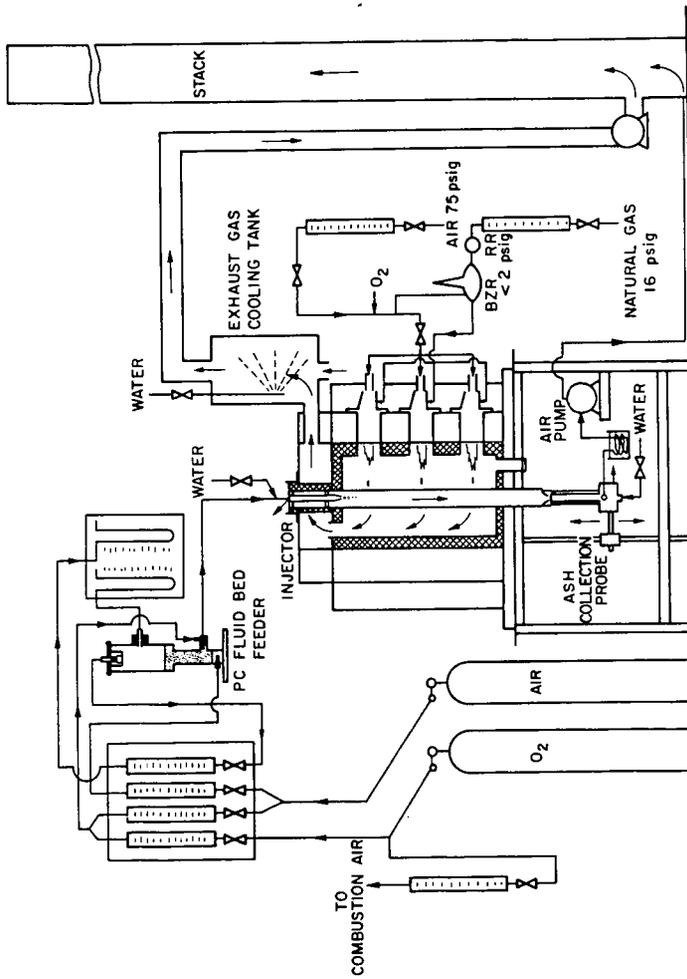
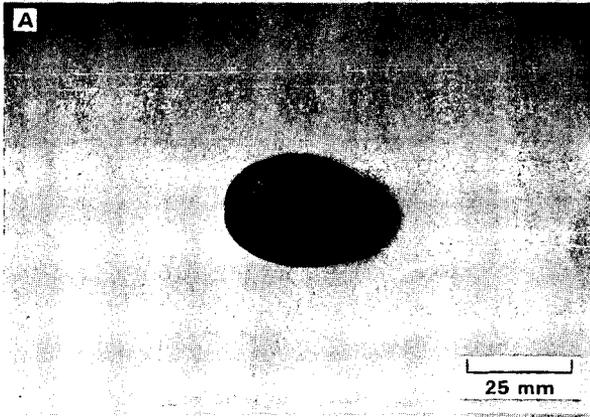


FIGURE 1 DROP-TUBE FURNACE SYSTEM



**FIGURE 2 RAW DECKER COAL ASH DEPOSIT:
A) TOTAL DEPOSIT AFTER TWENTY MINUTES,
B) OPTICAL PHOTOMICROGRAPH OF BONDED
ASH PARTICLES**

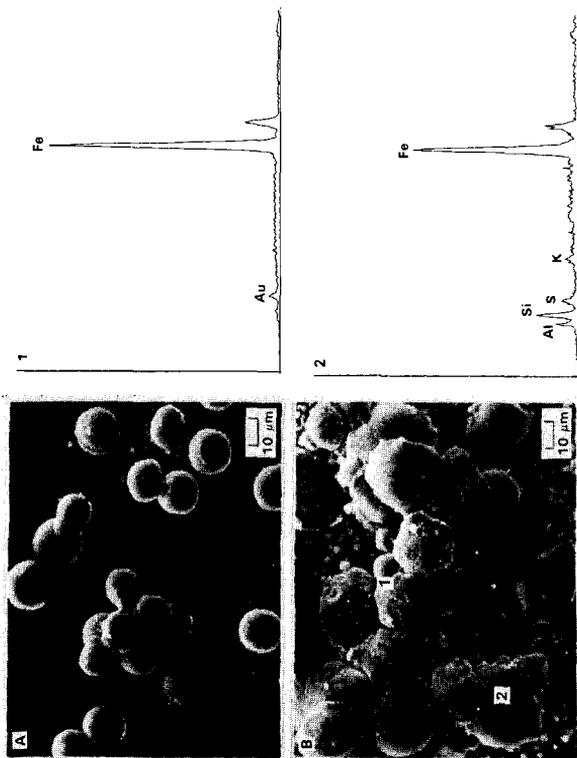


FIGURE 3 KEYSTONE COAL ASH DEPOSITS: A&B) SEM PHOTOMICROGRAPHS SHOWING IRON-RICH SLAG DROPLETS COLLECTED FROM FLAME TEMPERATURES OF 1470°C (A) AND 1550°C (B). X-RAY FLUORESCENCE SPECTROGRAMS CORRESPONDING TO POINTS 1 AND 2 IN PHOTO B.