

CHARACTERISTICS OF ASH AGGLOMERATES FROM AN ASH-AGGLOMERATING GASIFIER

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INTRODUCTION

An ash-agglomerating fluidized-bed gasifier has been under investigation at the Institute of Gas Technology (IGT). In such a process, carbon utilization can be substantially improved over that obtained when ash is removed by continually discharging a nonselective portion of the fluidized bed containing both ash and carbon.

The pilot plant gasifier has a diameter of 4 feet and operates at near atmospheric pressure. The schematic diagram of Figure 1 shows that agglomerated ash leaves the gasifier through a centrally located venturi tube through which part of the gaseous feed (steam plus air or oxygen) is introduced to the reactor. Details of the gasifier and its operation have been described by Sandstrom, Rehmat, and Bair in a recent paper (8). In the present paper, we describe the agglomerated ash obtained during gasification of coke breeze and FMC char, and we discuss the probable mechanisms of their formation.

EXPERIMENTAL

Petrographic samples were mounted, sectioned, and polished mostly according to methods employed in coal petrography (1). Our apparatus for microscopical observations and determination of reflectance has been described (4).

Iron oxides and sulfides can usually be recognized by appearance, especially when more than one oxide or sulfide is present. Ferrous sulfide is brilliant, though not as brilliant as pyrite, and has a yellowish cast. Ferrous oxide is dead white, while magnetite is darker and gray in color. In initial observations and if doubt is aroused, measurement of reflectance is useful. Reflectance in air is used in ore petrography. Our own approximate measurements with oil immersion, arranged in order of increasing reflectance, are shown below, together with literature values for reflectance in air. Values for some of the compounds can vary with orientation and composition.

<u>Mineral or Compound</u>	<u>Formula</u>	<u>Reflectance</u>	
		<u>In Air (3)</u>	<u>In Oil (Approx)</u>
		%	
Iron Spinel	FeO·Al ₂ O ₃	--	0.9-1.2
Magnetite	Fe ₃ O ₄	21.1	7-8
Ferrous Oxide	Fe _{1-x} O	--	18-24
Ferrous Sulfide	Fe _{1-x} S	42	18-24
Pyrite	FeS ₂	54.5	33-44
Iron Metal	Fe	--	40-50

Scanning electron microscopy was carried out under the direction of Dr. Oom Johari at IIT Research Institute.

Ash samples were analyzed by the lithium borate fusion method of Boar and Ingram (2), with aluminum, calcium, iron, silicon, and titanium finished by atomic absorption and with sodium and potassium by flame emission. Sulfate was determined by the Eschka method. Acid-soluble iron was extracted by boiling with 3N hydrochloric acid and was determined by atomic absorption.

Agglomerated Ash From Coke Breeze

The ash product consisted predominantly of well-rounded particles (beads) ranging from about 1/16 to 1/4 inch in diameter, sometimes accompanied by some angular coke particles (Figure 2a).

Beads from an early run (No. 17) were subjected to detailed examination. The air-to-steam ratio in this test was about 4:1 by weight; temperature in the fluidized bed ranged from about 1880^o to 1930^oF.

For microscopic observation the beads were mounted in epoxy resin, sectioned, and polished. A composite photomicrograph of a whole 1-inch briquet, taken with vertical illumination, is shown in Figure 3. Residual coke appears as light areas here, both as the main constituent of the angular particles and as the very small constituent particles of the rounded beads. These small particles are situated mostly on the periphery of the beads, although a few are buried in the interior.

The many rounded black areas in the bead are empty vesicles. Others, connected by passageways to the exterior, were filled with the epoxy resin during mounting. (The system is evacuated before covering the sample with the resin, and the liquid resin is forced into some of the vesicles by the readmitted atmospheric pressure.)

A composite photomicrograph of the same briquet taken with oblique illumination is shown in Figure 4. With this illumination, the continuous phase of glassy, melted ash in the rounded beads can be distinguished from many of the embedded, unmelted particles.

We did not attempt to identify all of the unmelted ash particles; however, we think that some with high reflectance are probably particles of high-alumina refractory from the walls of the unit. When the reflectances of some of these high-reflectance particles were measured, they agreed with that of the similarly mounted refractory. Very small vesicles in the melted ash appear as pinpoints of reflected light. Some of the large, empty vesicles are partly illuminated on one side.

The distribution of the residual carbon indicated by microscopic observation was substantiated by further investigation: A sample of the residue was separated by hand into beads and angular particles; analyses for carbon then showed only 1.9 weight percent in the beads and 70.4 weight percent in the angular particles. That most of the residual carbon in the beads is not embedded and is available for reaction was shown by igniting a sample of the beads for 1/2 hour at about 1550^oF, followed by an analysis for unburned carbon. Only 0.36 weight percent remained.

The surface energy of a melt (or solid) of this kind is high compared with that of carbonaceous solids, and thus melted ash does not wet or spread on the low-energy surface of the coke (7). This is confirmed by the observation (under the microscope) that coke particles appear to float on the surface of the glassy phase, as shown in the photomicrograph of Figure 5. The observed apparent contact angle between coke and the glassy phase varied from about 90 degrees to much more than that. This explains why so little coke is entrapped inside the melted ash.

We investigated the composition of the continuous or melt phase of the beads. Microscopic observations of polished sections (at higher magnification than shown in Figures 3 and 4) show the presence of crystals. The view in the photomicrograph of Figure 6 is typical, but occasional areas are found where the crystals are larger and comprise a larger fraction of the crystal-in-glass composite. Occasional particles of ferrous oxide and metallic iron have also been found and identified by measuring their reflectance. X-ray emission spectra of the crystals, obtained with a scanning electron microscope, indicated presence of iron and aluminum. Iron, aluminum, and silica were similarly identified as the major components of the matrix or continuous phase; titanium, potassium, and calcium were also detected in it.

It is well known that the fusibility of ash containing substantial amounts of iron (from pyrite in the original coal) depends on the oxidation-reduction potential of the atmosphere. The presence of occasional particles of metallic iron in the beads indicates that the atmosphere in at least some zones of the bed was reducing enough for reduction of ferrous oxide, although the product gas generally had too low a carbon monoxide-carbon dioxide ratio to expect such reduction. The phase diagram for the $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ system in equilibrium with metallic iron is thus of interest for an understanding of the ash behavior.

The phase diagram of Osborn and Muan (6) for the $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ system under this condition is shown in Figure 7. Note the narrow quadrilateral field for crystallization of iron cordierite, $2\text{FeO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$. The minimum liquidus temperature in the presence of hercynite ($\text{FeO}\cdot\text{Al}_2\text{O}_3$) and fayalite ($2\text{FeO}\cdot\text{SiO}_2$), at the lower left corner of the field, is $1990\pm 9^\circ\text{F}$. However, iron cordierite tends not to crystallize in the absence of seed crystals, and instead a metastable eutectic of fayalite, hercynite, and tridymite may form at $1963\pm 9^\circ\text{F}$ (5). In the presence of impurities, still lower liquidus temperatures may occur. Thus, Snow and McCaughy, working with mixtures prepared from clays containing impurities, found a liquidus temperature of 1778°F for this eutectic (9). However, no crystals typical of a eutectic were seen either by optical or scanning electron microscopy, nor was any fayalite detected by X-ray diffraction. Instead, it appears that a glass is formed when the melted ash cools.

Agglomerated Ash from FMC Char

The FMC char was much more reactive than the coke breeze, resulting in a lower bed temperature with comparable gas feed. On the other hand, more severe operating conditions (higher temperature or higher ash content of the bed) were required to obtain agglomerates large enough to be discharged automatically and in sufficient quantity to maintain the ash content of the bed in a steady state without periodic dumping. Steam had to be eliminated from the gas feed to obtain the required temperatures.

Agglomerated particles from two runs operating with FMC char as feed (Nos. 57 and 60) were examined. The feed for the first of these runs had been prepared from Illinois coal and that for the latter from Western Kentucky coal.

The agglomerated ash particles differed considerably from those produced from the coke breeze, being smaller and subangular instead of well-rounded. Particles from Run 60 are shown in Figure 2b with small beads from coke for comparison. In polished sections under the optical microscope, the clay of the coal ash appeared to be well-sintered, but no ferrous aluminum silicate was detected by X-ray emission in the scanning electron microscope. Instead, the iron appeared mostly in the form of ferrous sulfide and magnetite. In both feed chars, the iron appeared as ferrous sulfide; in the agglomerated ash from an early period of Run 57, some magnetite had appeared, but most of it was ferrous sulfide, much of it as separate particles. Some was occluded in the agglomerated

clay as dispersed, 1 to 10- μ m particles, and some had spread over the surface of the clay particles as shown in Figure 8. In the agglomerates from a later period of the run, much of the exposed iron, but not the occluded particles, had been converted to magnetite. In the agglomerated ash from a late period of Run 60, a portion of the magnetite on the outer zone of the particles had been reduced to wüstite (FeO). Rings of ferrous sulfide, similar in shape to those found on separate particles, were observed in the interior of the agglomerates. Formation and automatic discharge of these agglomerates occurred in Run 60 with a bed temperature of about 1950°F and an ash content of about 50% in the fluidized bed.

DISCUSSION

Differences in elemental composition among the three feed materials (Table 1) are probably not very significant in interpretation of the agglomeration process; however, analysis for acid-soluble iron indicated that a large part of the iron in the coke had already reacted with the clay minerals to form the acid-insoluble, low-melting ferrous aluminosilicate. (Pyrite also is insoluble in hydrochloric acid but is decomposed or oxidized in the preparation of the coke and char. Soluble iron compounds occluded in sintered clay also do not dissolve.)

Table 1. PROPERTIES OF ASH IN COKE AND CHAR FEEDS

Elemental Composition, wt %	Coke	FMC Char	
		From Ill. Coal	From Ky. Coal
SiO ₂	47.1	35.7	39.9
Al ₂ O ₃	20.8	17.5	23.4
Fe ₂ O ₃	18.9	24.1	24.1
TiO ₂	0.81	0.88	0.51
CaO	3.25	3.50	0.43
MgO	1.01	0.85	0.74
Na ₂ O	0.54	4.03	0.60
K ₂ O	1.72	2.48	0.65
SO ₃	2.26	5.15	1.95
Total	96.4	93.4	92.3
Acid-Soluble Iron, % of total iron	47	98	97
Ash Fusibility, °F			
Reducing Atmosphere			
IT	2085	1780	2005
ST	2155	1950	2050
HT	2230	1980	2080
FT	2440	2160	2340
Oxidizing Atmosphere			
IT	2510	2215	2475
ST	2630	2300	2520
HT	--	2360	2540
FT	--	2500	2560

Thus, two different modes of ash agglomeration are indicated, namely, iron oxide fluxing (formation of molten ferrous aluminum silicate), and, under more severe conditions, clay sintering. Possibly the presence of relatively low-melting (and thus prone to sintering) ferrous sulfide (mp 2180°F) on the exterior of clay particles may have aided in their agglomeration.

Prediction of the performance that will be obtained with other types of feed is uncertain. The form of the iron in the feed is obviously important; iron in hydrogasification residue, for example, is likely to have been converted to ferrous oxide and would thus be in a much readier form to react with and flux the clay than it is in char. This may also be the case even with raw coal as the feed, because a gasification atmosphere has a higher oxidation potential than a pyrolysis atmosphere does.

ACKNOWLEDGMENTS

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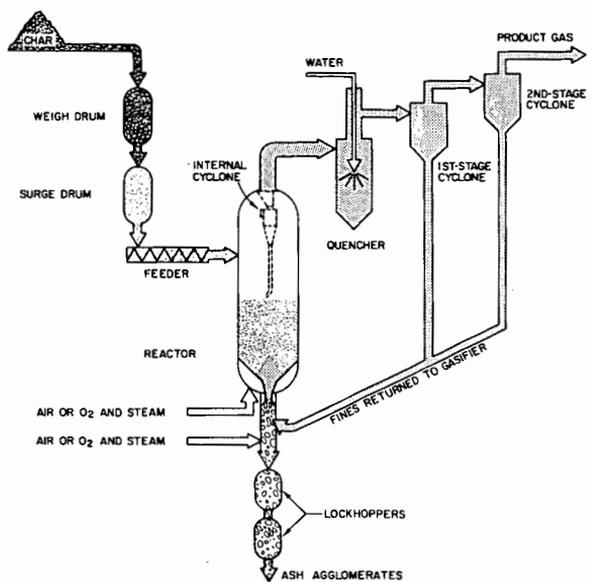


Figure 1. SCHEMATIC DIAGRAM OF ASH-AGGLOMERATING GASIFIER

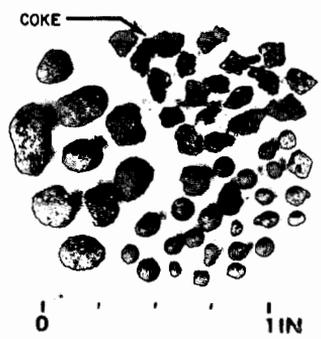


Figure 2a.
ASH AGGLOMERATES FROM
COKE, WITH COKE PARTICLES

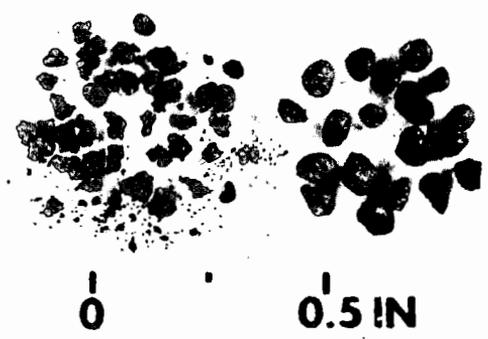


Figure 2b. ASH AGGLOMERATES FROM
FMC CHAR (Left), AND COKE (Right)

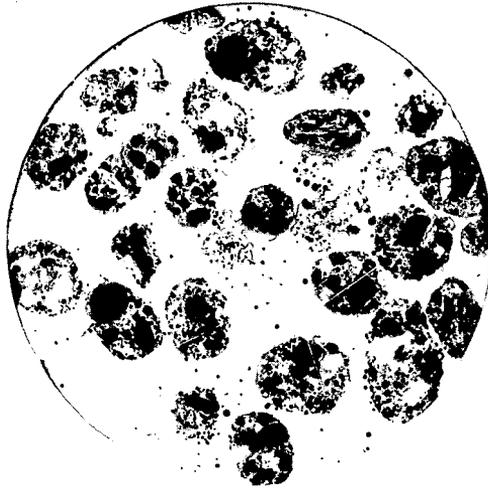


Figure 3. AGGLOMERATED ASH BEADS
FROM COKE - VERTICAL ILLUMINATION

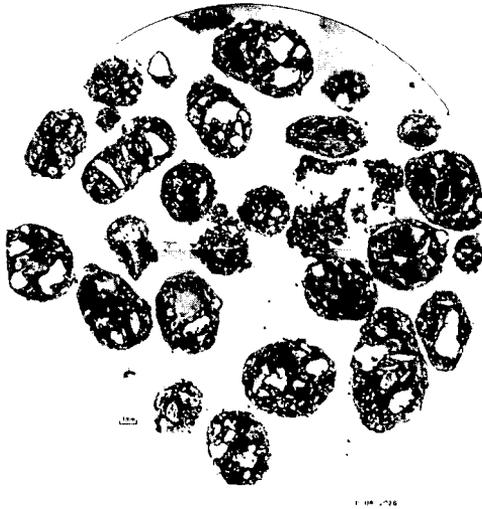


Figure 4. AGGLOMERATED ASH BEADS
FROM COKE - OBLIQUE ILLUMINATION

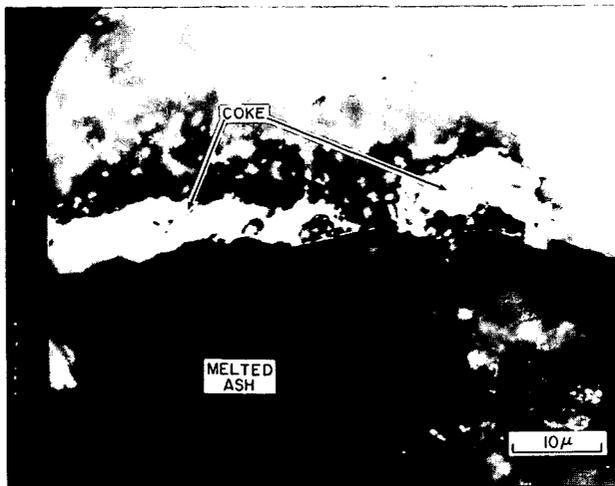


Figure 5. COKE PARTICLES ON SURFACE OF MELTED AND RESOLIDIFIED ASH OBSERVED BY OPTICAL MICROSCOPE WITH OIL IMMERSION

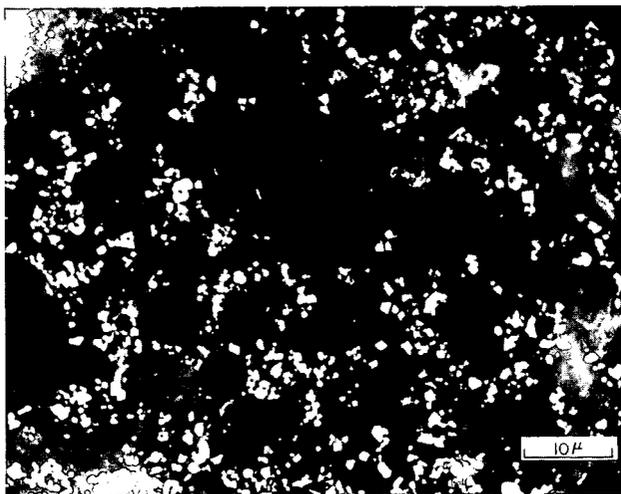


Figure 6. CRYSTALS OF HERCYNITE ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) IN MELTED AND RESOLIDIFIED ASH OBSERVED BY OPTICAL MICROSCOPE WITH OIL IMMERSION

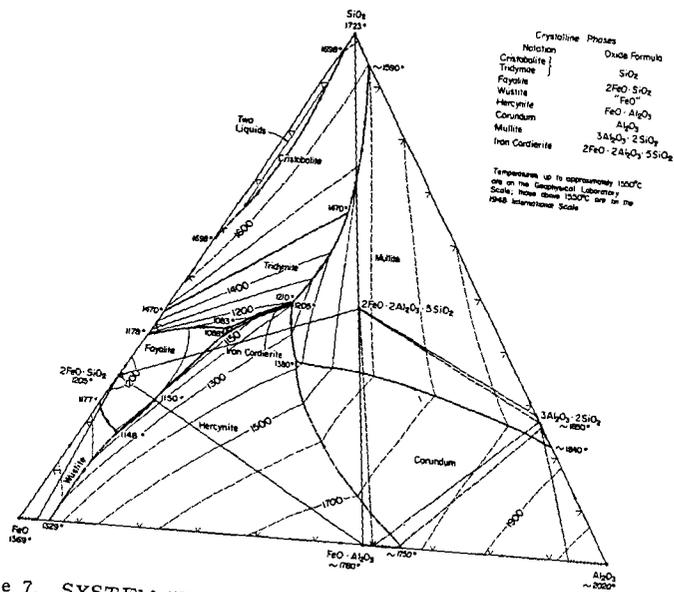


Figure 7. SYSTEM "FeO"-Al₂O₃-SiO₂; COMPOSITE, BY WEIGHT (Oxide Phases in Equilibrium With Metallic Iron)(6)

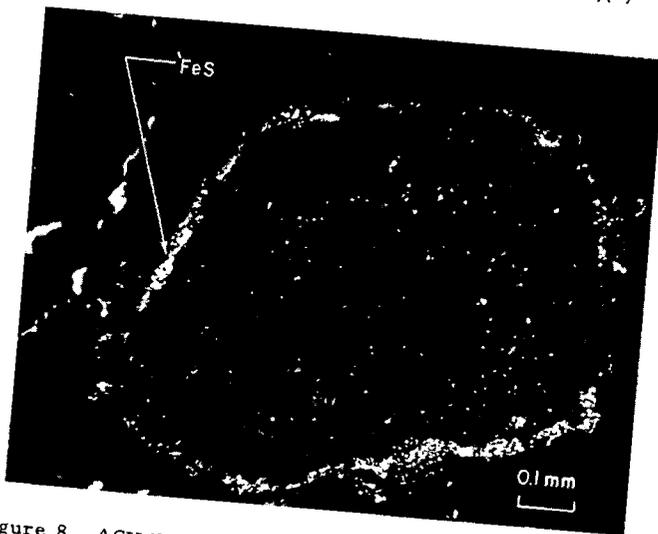


Figure 8. ASH PARTICLES FROM FMC CHAR SHOWING A COATING OF FERROUS SULFIDE ON SINTERED CLAY