FORMATION AND GROWTH OF COAL ASH AGGLOMERATES

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BACKGROUND

The behavior of the mineral matter of coal and its reaction product, ash, is of concern in gasification processes because it governs deposition on gasifier and downstream surfaces as well as agglomeration in ash-agglomerating gasifiers. In general, fluidized-bed coal gasifiers operate under backmixed conditions. Consequently, the gasifier solids drain stream could carry with it some unconverted carbon. In contrast, in the KRW and U-GAS processes, the high-velocity jet in the gasifier effectively agglomerates the ash, thereby facilitating its selective removal from the fluidized-bed, and thus achieving carbon conversion in excess of 98%.

The minerals in high-sulfur bituminous coal are predominantly pyrite, quartz, and clay minerals. The reactions of most importance in the formation of ash agglomerates are 1) the oxidation of the ferrous sulfide produced by the decomposition of the pyrite and 2) the subsequent or simultaneous reaction of the resulting iron oxide with the clay minerals and quartz to produce relatively low-melting iron aluminosilicates that form the matrix material for the ash agglomerates. For the ash-agglomerating fluidized-bed gasifier, the iron oxidation and iron aluminosilicate formation occur in the jet region of the reactor due to its oxidizing atmosphere and elevated temperature.

In a fluidized-bed gasifier, the char particles that contain mineral matter may be divided into two groups. One group contains a combination of clays and quartz (the acids) and pyrite or other fluxing agents such as CaO, MgO, Na_2O, and K_2O (the bases) that will form a low-melting aluminosilicate agglomerate as the carbon in the particle is gasified. The second group of particles contain either a single type of mineral matter or very small amounts of pyrite or the other fluxing agents and lead to the formation of "free ash" that does not melt as the char is gasified. Agglomerate growth occurs both by combination of the smaller molten agglomerates and by capture of the free ash by the molten agglomerates. Therefore, the tendency of a coal to form ash agglomerates should be dependent on both the distribution of the mineral matter as well as its average composition.

Coal Mineral Matter: The overall aim of the IGT ash chemistry studies is to predict the behavior of the coal ash in a fluidized-bed gasifier on the basis of a minimum analysis of the characteristics of the feed coal mineral matter and the operating conditions of the gasifier. In this study the objective was to correlate the composition and distribution of the mineral matter for five eastern and two western coals to the behavior of their ash in a laboratory gasifier. The choice of the eastern coals was limited to washed products to concentrate on the initial phases of ash reactions — those of the ash brought into juxtaposition for reaction by the gasification of the carbon of individual particles.

Coals were sought whose ash composition would reflect the full range of the most important variable for agglomeration, the average concentration of pyrite relative to the siliceous minerals. The concentration of calcium minerals — typically calcite — is probably next most important variable. Accordingly, we selected four U.S. bituminous coals covering a wide range of iron oxide and only

small amounts of calcium oxide in the ash. An Illinois No. 6 Seam coal with high calcium oxide and low iron oxide, a western bituminous (York Seam), and a subbituminous coal (Rosebud Seam) were also selected for testing.

The mineral matter in each coal was characterized by: determination of the concentration of major and minor oxides in the ash; Mossbauer analyses to measure the concentration by type of the iron compounds present; and mineralogical analyses by computer-assisted scanning electron microscopy (SEM).[1,2] Typically, in the eastern bituminous coals, iron is present as pyrite and its oxidation products, namely sulfates. In the York coal, the iron is mainly present in chamosite and in siderite.

MINERAL MATTER DISTRIBUTION

For this study, a method of characterizing the distribution of the mineral matter of coal was developed. Of interest here is a practical method of determining how much of the ash of the coal yield slag of viscosity low enough for agglomeration as the char of single particles becomes completely gasified. Most important are the iron and calcium oxide contents of the ash in relation to silica plus alumina. For this investigation, the ash compositions of 32 single particles of the coals were determined chemically. Particles from the -10+12 mesh fraction of the coal were taken for analysis; this size furnishes enough ash for the chemical analysis and is about the average size, by weight, of the coal feed to a pilot plant or commercial fluidized-bed gasifier. Particle weight, ash content, and iron oxide and calcium oxide in the ash were determined. Also, the concentration of basic constituents (BC) was estimated for each particle. The estimation, which included a correction for sulfate in the particle ash, was deemed to be satisfactory on particle ashes containing less than about 20% CaO.

The agreement, or lack thereof, of the average calcium oxide and iron oxide contents of the ash of the particles with those found by the conventional analyses (Table 1) was significant in the behavior of the mineral matter in agglomeration. For example, although the average iron oxide in the ash of the 32 particles of Kentucky No. 9 coal agrees well with the conventional analysis, less than half as much calcium oxide was present in the -10+12 mesh particles as in the conventional analysis. Evidence indicates that the missing calcium oxide occurs as calcite in the cleat of the coal, along which fracture occurs in crushing, and that loss of the calcite by attrition from coal particles occurs in crushing and sieving, resulting in its concentration in the finer sieve fractions. The presence of plates of calcite, about 10 μm thick, in the cleat fractures of the Kentucky No. 9 coal was found by macroscopic examination of LTA-etched coal sections oriented perpendicular to the bedding.[1]

A loss of almost 90% of the calcium oxide from the -10+12 mesh particles is evident with the Indiana VI and Illinois No. 6 coals. No loss, or only a marginal one, is evident from the Pittsburgh No. 8 or Kentucky No. 13 coals. Nor did it occur with the subbituminous B Rosebud coal, in which the calcium occurs dispersed in the organic matter, partly as carboxylate and (probably) partly as calcite from decomposition of calcium carboxylates. However, about 90% of the average amount of iron oxide is abaent from the -10+12 mesh particles of this coal because of a similar occurrence of pyrite in the cleat.[3,4]

The distributions in particles larger and smaller than the -10+12 mesh also should be considered. In general, the distribution is expected to become wider (greater deviation from the average) as particle size decreases, and, for example, the number of particles with a single layer, whether attrital coal or vitrain, increases. The opposite may be true of larger particles, but not if the size of

particles is less than that of the predominant width of the layers. The appearance of the ashes of individual -4+5 mesh particles of the Kentucky No. 9 coal suggested that the distribution of iron in these particles does not differ much from that of the -10+12 mesh particles.[1]

At present, it is estimated that, in the absence of more than about 2 weight percent of calcium oxide, single-particle ash with iron oxide contents of between 15 and 80 weight percent may form a low-melting agglomerate after carbon burn-off without the need for combination with the ash of a different particle. A summary of the distribution of iron oxide in the ash of the -10+12 mesh particles is presented in Table 2 for the eastern bituminous coals, together with the bulk average iron oxide content. Ash of Kentucky No. 9 coal, from the same mine as that used here, agglomerated without difficulty in U-GAS pilot-plant tests with bed temperatures at about 1870°F and substantially higher temperatures in the jet. The particle analyses of this coal show 44% of the ash to have 0 to 15 weight percent Fe_2O_3 and 53% to have 15 to 80 weight percent Fe_2O_3. Although the ash of the Pittsburgh No. 8 coal has an average Fe_2O_3 content of 31.7 weight percent, much higher than that of the ash of the Kentucky No. 9; its fraction of ash in the 15 to 80 weight percent Fe_2O_3 range is much lower, only 12%. This indicates that the ash of the Pittsburgh coal should agglomerate more slowly. The same is true of the Indiana VI coal, whose ash has overall sufficient iron, 15.7 weight percent Fe_2O_3, for agglomeration, although very little falls in the 15% to 80% range. The Kentucky No. 13 and Illinois No. 6 coals probably have insufficient iron for agglomeration of their ash, but if so, the ash content of the bed in a gasifier can be allowed to rise to such an extent that almost all of the carbon is gasified.

EXPERIMENTAL

In the batch gasification tests used in this work, chars rather than coals were used to prevent caking of the coal particles. The preparation of the chars for the gasification tests is described in detail elsewhere.[2] The preparation of char from each coal was identical except for a sample of the Kentucky No. 9 coal that was prepared as a test of the effect of uniformity of distribution of the coal mineral matter on ash agglomeration. This sample of coal was first ground to -200 mesh to more uniformly distribute the coal mineral matter, and then it was devolatilized. During devolatilization, the coal agglomerated to form a bulk sample of char. This char was then ground and sized similar to the other char samples used in the agglomeration tests.

For the ash agglomeration tests of these coals, a previously constructed 2-inch-diameter fluidized-bed gasifier with a center jet configuration was used. A fluidizing gas of nitrogen and steam was introduced through a perforated metal disk at the bottom of the reactor and air was fed through the center jet to produce a hot region within the fluidized-bed where the temperature may be as much as 200° to 300°F higher than the temperature of the bed. Each test used a charge to the reactor of 100 g of coal char. The testing was standardized at a steam-to-oxygen molar ratio of 2:1, a bed temperature of 1950°F, and a superficial gas velocity of between 1.3 and 2.0 ft/s.

Before preparation of aliquots of the residues of the gasification tests, any clinker obtained was crushed to pass an 8-mesh sieve and was mixed with other residue. One portion of the residue was riffled and used for estimation of agglomerate content. This portion was ashed at 900° to 1100°F in a muffle furnace for at least 20 hours to remove carbon and achieve better visibility of the mineral matter. The temperature of ashing is high enough to burn off the carbon but low enough to avoid further reactions of the mineral matter, other than oxidation of the ferrous sulfide. The agglomerates, free ash, and pieces of clinker that are

isolated by the combustion of the carbon in the reactor residue were then sieved and each sieve fraction examined visually under a low-power microscope to estimate the amount of agglomerates.

A point-count analysis was also performed on the residues. Fractions of the ash coarser than 325 mesh were combined for this purpose, mounted in epoxy resin containing a yellow pigment, and polished. Removal of most of the material resulting from ashing of the char, consisting of fine grains, was essential to facilitate the point-count. Particles containing any matrix material, identified by occurrence of vesicles and usually by low reflectance, were counted as agglomerates; all others were counted as free ash, which was then augmented by the addition of the -325 mesh fraction. For the present purposes, the point-count was taken to be proportional to weight percent. Other details of the procedure are reported elsewhere.[2]

RESULTS AND DISCUSSION

A summary of results obtained for the agglomerate content of the ashed residues is presented in Table 3; this table includes agglomerate contents of ash from completely gasified char, calculated on the assumption that the quantity of this ash is proportional to the carbon conversion. In Table 3, excellent agreement is shown between agglomerate contents of the ash by inspection of sieve fractions and by point-count for tests on the Kentucky No. 9, Pittsburgh No. 8, and Illinois No. 6 chars in which no clinkers were produced, and also in tests on the fine-ground Kentucky No. 9, Indiana VI, and Illinois No. 6 in which clinkers were produced.

A comparison of agglomerate contents of ash from completely gasified chars for the tests on the Pittsburgh No. 8 and Illinois No. 6 chars, with and without clinkering, indicates that clinkering increases the agglomerate content. The average percent of agglomerate content obtained without clinkering is 65% to 71% of the agglomerate content obtained with clinkering; depending on the inclusion or not of the low value for agglomerates found by examination of sieve fractions in the test on the Pittsburgh No. 8 char in which clinkering occurred. With application of the correction, the "best" estimate of agglomerates obtained from the fine-ground Kentucky No. 9 is 60% to 66%, and from the Indiana VI is 61% to 67%.

An important step in the agglomeration of ash is the reaction of iron compounds with siliceous ones to form iron aluminosilicates. In a U-GAS pilot-plant test, conversion amounted to as much as 82% of the total iron, according to a Mossbauer analysis of the ash discharge. In the gasification tests reported under the previous program in which a central jet was not used, only a minor amount of iron aluminosilicate was formed.[4,5] With the addition of a central jet tube through which the oxygen is introduced, the tests on bituminous coal chars reported here show formation of iron aluminosilicate mostly in the range of 50% to 80% of the iron, as shown by the Mossbauer analyses.[1]

In the present series, the low conversion of iron to aluminosilicate in the Rosebud char can be attributed to the occurrence of pyrite both in the cleat and as large particles. Both of these factors can be expected to make conversion of iron to aluminosilicate less likely.

For the eastern coals, the best estimate of the agglomerate content of ashed residues in Table 3 gives an overall indication of their initial agglomeration potentials. It is noteworthy that these agglomerate amounts from completely gasified char range from only 38% to 66%, whereas the iron oxide of the ash of these coals ranges from 8% to 32%. An explanation is that the agglomerates from the coals with low iron oxide (the Kentucky No. 13 and the Illinois No. 6) in comparison to

the Kentucky No. 9, contain a substantially greater proportion of clay-derived material engulfed in or attached to the iron aluminosilicate matrix material.

It is also noteworthy that the agglomerate content of the ashed residue from the fine-ground Kentucky No. 9 coal was greater than that of the residues from the usual preparation. In the usual preparation, 1/4-in. top size coal was devolatilized and the resulting char was crushed to pass an 8-mesh sieve, whereas for the fine-ground tests the same coal was ground to pass a 200-mesh sieve before charring. The particle-by-particle distribution of iron in the char made by the usual preparation is probably well-represented by the data of Table 2, according to which 53% of the ash had from 15% to 80% Fe_2O_3. The expected effect of the fine grinding is to cluster the iron content of the ash of the particles of char more closely around the average 20% of Fe_2O_3 in the ash of this coal (Table 2). The test results indicate that this distribution is better for agglomeration than that of the original Kentucky No. 9 coal. These results and those on the Kentucky No. 13 coal indicate that ash containing as little as 10% Fe_2O_3 contributes to agglomeration. However, the resulting iron aluminosilicate may have a higher iron content because reaction with the siliceous minerals is incomplete.

The agglomerate content of the ashed residue from the Pittsburgh No. 8 char was only equal to that of the Kentucky No. 9, in spite of the substantially higher average iron oxide content of its ash — 31.7 versus 19.9 weight percent. This is attributed to the isolation from siliceous minerals of much of its pyrite, as shown by the iron oxide distribution where only 12 weight percent of the ash had between 15% and 80% Fe_2O_3; the effect is substantiated by a detailed point count analysis of the residue from Run 1744-30, in which no clinker was formed and in which 40% of the unagglomerated ash was in the form of iron oxide.

Three residues were analyzed by computer-assisted SEM to investigate the effect of large amounts of calcium oxide in the ash: the low calcium Kentucky No. 9 for reference; the Illinois No. 6, a high-calcium eastern bituminous; and the Rosebud, a western subbituminous with about the same amount of iron oxide and calcium oxide in the ash as the Illinois No. 6. In the residues of the gasification tests, the ratio of weight of iron-containing silicate compounds to that of other iron compounds (oxide and sulfide) is roughly equal (10:1) for the Kentucky No. 9 and Illinois No. 6 tests, and is significantly lower (about 6:1) for the Rosebud char test. This trend agrees with the Mossbauer results, which were attributed to the large size of pyrite particles and its occurrence in the cleat of the Rosebud coal. The opposite is true of the calcium; all of it in the Rosebud char has reacted to form silicates, whereas a substantial part of the calcium in the Illinois No. 6 char has not reacted, as shown by a weight ratio of about 3:1 of calcium silicates to other calcium compounds. The ratio of calcium reacted with silica to unreacted calcium would be even lower. Here again, a mineral in the cleat — calcite of the Illinois No. 6 coal — has reacted with siliceous minerals to a lesser extent than the well-distributed calcium — calcite and carboxylate — of the Rosebud coal.

The analyses for agglomerates in the residues from the Rosebud char show poor agreement, for which no explanation is apparent; no clinker was formed in either of two tests. According to the SEM analysis, the calcium oxide did react to form silicates and aluminosilicates, which should yield slag of about the same viscosity as a slag that would result if the calcium oxide had been iron oxide. As noted previously, the pyrite in this coal has been reported to occur in relatively large grains and, at the 30 mesh level of crushing, to be unattached to coal. Hence, the small amount of iron in the ash (7.0 weight percent Fe_2O_3) may also be less reactive than usual, similar to part of the iron in the Pittsburgh No. 8 coal.

Iron and calcium oxides in the York coal were each slightly higher than in the Rosebud, but the iron is mostly in a clay mineral and thus probably evenly distributed among all the siliceous minerals; as a result, the formation of iron calcium aluminosilicates of higher than average iron and calcium content would be much less favorable than when the iron is present as a discrete phase, as in the other coals.

In summary, the following conclusions have been made based on these results:

- A particle-by-particle method of chemical analysis can be used to determine the distribution and association of minerals in the coal feed to fluidized-bed gasifiers.

- With few exceptions, in gasification tests in which oxygen was introduced through a central jet and the fluidized bed was maintained at 1950°F, a major part of the iron was converted to iron aluminosilicates irrespective of a wide range of iron content from 10 to 32 weight percent Fe_2O_3 in the ash.

- Consistently low conversion of iron to aluminosilicate in the case of the subbituminous Rosebud char can be attributed to the large size of the pyrite and its occurrence in the cleat of this coal. A greater fraction of the calcium of the Rosebud coal, in which the calcium is uniformly distributed, was converted to silicates than was that of the Illinois No. 6 coal, most of which occurs in the cleat. Analyses also confirmed that a greater fraction of the iron of the Kentucky No. 9 and Illinois No. 6 coals was converted to silicates than was that of the Rosebud, most of which occurs in the cleat. This shows that calcite and pyrite that occur in the cleat and separate as free ash during grinding are less likely to form ash agglomerates.

- The results of the gasification tests performed in this study indicate that in individual coal particles Fe_2O_3 concentrations between 15 and 80 weight percent of the ash promote the formation of ash agglomerates, whereas ash outside this range tends to form free ash rather than agglomerates.

- In the gasification of coals of low-iron-content ash, significant formation of ash agglomerates can occur by the joining of unmelted mineral matter with relatively small amounts of the iron aluminosilicate matrix material.

- Characterization of the composition and distribution of the coal ash using the techniques developed in this study could be of assistance in setting the operating conditions of fluidized-bed, ash-agglomerating gasifiers.

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Table 1. SUMMARY OF AVERAGES OF SINGLE-PARTICLE ANALYSES

	Ash (Moist Basis)		Fe_2O_3 in Ash		CaO in Ash	
	Avg. of Particles (Range)	Bulk Avg.	Avg. of Particles (Range)	Bulk Avg.	Avg. of Particles (Range)	Bulk Avg.
	wt %					
Kentucky No. 9	6.3 (0.4-32.8)	7.6	22.3 (3.3-98.1)	19.9	1.10 (0.41-19.2)	2.29
Pittsburgh No. 8	10.9 (1.0-42.1)	7.5	34.2 (0.7-91.0)	31.7	1.14 (0.25-28.2)	0.90
Kentucky No. 13	8.2 (0.3-21.2)	7.3	8.6 (0.8-52.8)	8.1	0.69 (0.17-11.5)	0.90
Illinois No. 6	10.3 (1.1-32.5)	11.9	12.1 (1.8-91.7)	10.7	0.83 (0.21-14.0)	8.34
Indiana VI	16.4 (0.6-56.6)	13.4	6.9 (2.0-81.7)	15.7	0.36 (0.10-20.3)	2.48
Rosebud	10.3 (2.1-45.8)	11.3	0.55 (0.1-6.14)	7.0	9.4 (1.95-45.3)	7.2

Table 2. SUMMARY OF DISTRIBUTION OF Fe_2O_3 IN -10+12 MESH PARTICLES OF EASTERN BITUMINOUS COALS

Coal	Fe_2O_3 Content Bulk Avg.	Fe_2O_3 Content Particle Avg.	Distribution of Fe_2O_3 Concentration in All Particle Ashes: 0-15% Fe_2O_3	15-80% Fe_2O_3	80-100% Fe_2O_3
	wt%		% of all particle ashes		
Kentucky No. 9	19.9	22.3	44	53	3
Pittsburgh No. 8	31.7	34.2	59	12	29
Kentucky No. 13	8.1	8.6	89	11	0
Illinois No. 6	10.7	12.1	82	16	2
Indiana VI	15.7	6.9	91	9	0

Table 3. SUMMARY OF AGGLOMERATE CONTENT OF ASHED RESIDUES FROM 2-INCH-ID GASIFICATION TESTS BY POINT-COUNT AND SIEVE ANALYSIS

Coal	Basic Constituents, wt %	Dolomite Ratio	Test No.	Carbon Conversion, wt %	Clinker Formed	Agglomerate Content of Ashed Residue, wt %: In Total Ash: By Point-Count	In Total Ash: On Sieve Fractions	In Ash From Completely Gasified Char: By Point-Count	In Ash From Completely Gasified Char: On Sieve Fractions	Best Estimate
Kentucky No. 9	26	12	1744-06	63	None	36	35	57	56	57
			1744-07	73	Small amt.	--	46	--	63	
Kentucky No. 9 Fine-Ground	26	12	1744-14	83	1.2 g	76	77	92	93	60-66[a]
Pittsburgh No. 8	35	4	1744-08	74	1.35 g	62	48	84	65	57
			1744-30	51	None	26	29	56	57	
Kentucky No. 13	13	16	1744-12	78	2.8	36[b]	19	53[b]	24	~38[a,b]
			1744-15	46	1.2	33[b]	24	61[b]	45	
Illinois No. 6	24	41	1744-17	61	Yes	38	40	62	65	41
			1744-20	55	None	22	23	39	42	
Indiana VI	24	16	1744-21	53	3.4 g	55	50	100	94	61-67[a]
York	23	50	1744-23	64	None	22	8	34	13	~23
			1744-29	64	None	--	14	--	22	
Rosebud	19	57	1744-26	75	None	--	40	--	53	--
			1744-27	67	None	23	10	31	15	

[a]Corrected for the effect of clinkering as shown by the tests on the Pittsburgh No. 8 and Illinois No. 6 coals.

[b] Includes much clay with small amounts of attached iron aluminosilicate.

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