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Bed Material Agglomeration During Fluidized Bed Combustion

Technical Progress Report for the Period
July 1, 1993 - September 30, 1993

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Abstract

During this quarter, agglomerates formed in laboratory coal combustion tests were analyzed to determine the chemical and mineral reactions which lead to the cohesion of bed particles. Combustion tests were conducted at 75%, 90%, 100%, and 120% theoretical air values. The test at 75% theoretical air resulted in the formation of bed agglomerates within 30 minutes.

Agglomerates which formed at the lower theoretical air values were compared to unagglomerated bed samples by x-ray diffraction analyses (XRD). Polished thin sections of the agglomerates were made for optical and scanning electron microscopy. Polarized-light microscopy was performed using a Zeiss research microscope. Individual particles were analyzed using an ARL electron microprobe and a JOEL 840 scanning electron microscope.

The results of these analyses indicate there were, in a broad sense, two types of mineralogic reactions which lead to the cohesion of bed particles in the agglomerates. One mechanism of cohesion resulted from the melting of bed particles to form a viscous material which bridged other bed particles. Based on the chemical composition of the glass (which resulted from the melt), this material was probably derived from aluminosilicate minerals in the sand bed or from clays within the coal. Because of the high iron content in these glasses (4 to 5 wt%), it is likely that iron pyrites in the coal were involved in fluxing reactions. In addition, MgO appears to be relatively high in the glasses. It is suspected that Ca-Mg carbonates (dolomite) from the bed sand are also involved in mineralogic reactions with the aluminosilicate melt.

The second type of mineralogic reaction appears to be a reaction involving calcium and magnesium with other bed particles and with the aluminosilicate melt to form new mineral phases. Although the composition of these phases is somewhat variable, some resemble single-chain silicates or pyroxenes.

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Objective

The purpose of this project is to determine the physical and chemical reactions which lead to the undesired agglomeration of bed material during fluidized bed combustion of coal and to relate these reactions to specific causes.

Progress

Laboratory Combustion Tests

Laboratory combustion experiments were conducted at 75%, 90%, 100%, and 120% theoretical air values. For the tests at lower theoretical air, bed expansion was maintained at the values of the 120% theoretical air tests by supplementing the fluidization air with nitrogen. Illinois No. 6 coal was used and the bed consisted of 30 x 40 U.S. mesh sand. During the combustion tests the bed temperature did not exceed 1550°F. Table 1 shows the test results for different values of theoretical air.

Table 1. Effect of excess air on agglomeration.

EQUIVALENCE RATIO	RESULT
1.20	no agglomeration
1.20	no agglomeration
1.00	no agglomeration
0.75	agglomeration
0.90	no agglomeration
0.75	agglomeration

Agglomerates which formed at lower theoretical air values were compared to unagglomerated bed samples by x-ray diffraction analyses (XRD) and polished sections of the agglomerates were made for optical and scanning electron microscopy. Polarized-light microscopy was performed using a Zeiss research microscope. Individual particles were analyzed using an ARL electron microprobe and a JOEL 840 scanning electron microscope.

Results and Discussion

There appear to be two types of reactions which lead to the cohesion of bed particles. Most of the cohesion of bed particles resulted from the melting (and/or softening) of an aluminosilicate material which flowed and bridged other bed particles. An additional type of reaction appears to result from reaction of calcium and magnesium-rich bed particles with both the melt and other bed particles, to form new mineral phases.

Figure 1 is a scanning electron back-scatter image of an agglomerate formed at 75% theoretical air. Back scatter electron images reflect the mean atomic number of the elements in any material. The darker the gray-tones the greater the mean-atomic number of the material. The black areas in the photo are void spaces in the agglomerate. In this photograph, the darker gray particles are quartz (SiO_2) and feldspar (Na-Ca-K aluminosilicates) particles from sand used for bed material. These particles have become cemented with a material which is primarily composed of silica and alumina. Figure 2 shows an example of new mineral phases formed within the melt and around bed particles. These reactions will be discussed later in this report.

Figure 3 is a comparison of the x-ray diffraction patterns of unagglomerated material (from 100% theoretical air test) and the sand used for the fluidization bed. From the x-ray diffraction patterns, it can be seen that the mineralogy of the bed material is dominated by the composition of the sand. Based on this data, the bed sand consists of quartz, various fledspar minerals (Na-Ca-K aluminosilicates), and dolomite (Ca-Mg carbonate). The carbonate peak is not present in the agglomerate, probably due to the calcining of this mineral during combustion.

Figure 4 is a comparison of x-ray diffraction patterns of agglomerates from a test at 75% theoretical air and unagglomerated material from a test at 100% theoretical air. Based on x-ray diffraction data and optical microscopy, the agglomerated samples differ from the unagglomerated samples in several ways. First, it appears some of the bed material (and coal ash) has been melted and has flowed around other bed particles. After cooling, the melt formed a glass which is easily identified using polarized-light microscopy. This glass can also be seen in the x-ray diffraction patterns as a "hump" in the background spectra between 15 and 35 2-Theta (See Figure 4 , 75% theoretical air). The composition of the melted material was characterized by electron microprobe and was found to be somewhat variable. Compositions along a traverse of a grain of bed material into the glass are given in Table 2.

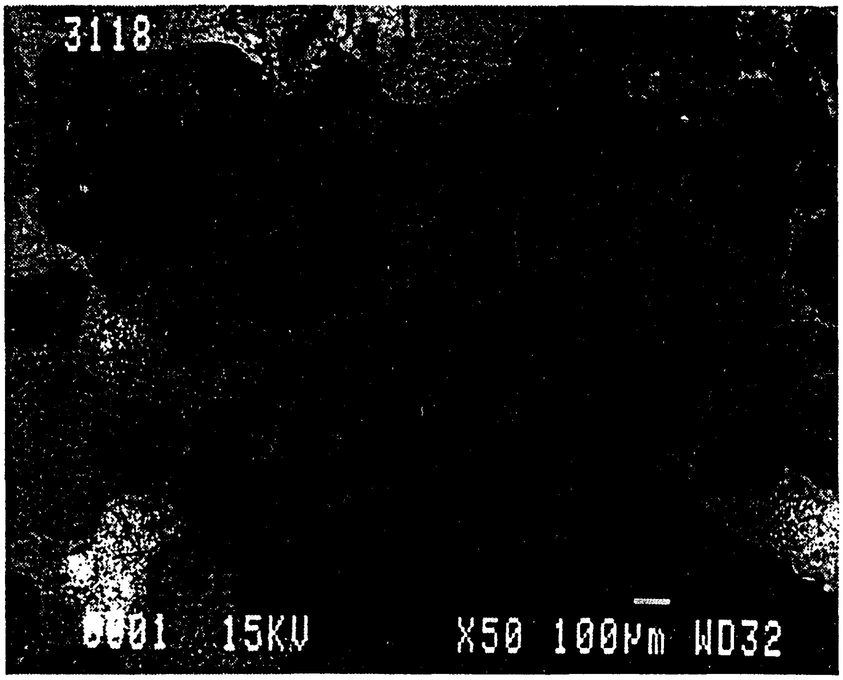

Figure 1. Scanning electron photograph (back-scatterd electrons) of agglomerated bed particles. Darker areas contain materials with higher atomic numbers. The darker gray areas are bed particles which have been cemented together by the lighter gray material. Black areas are voids. See text for discussion.

Figure 2. Photomicrograph showing mineral reactions around quartz grains in the agglomerated bed material. Field-of-view is 0.7mm. See text for discussion.

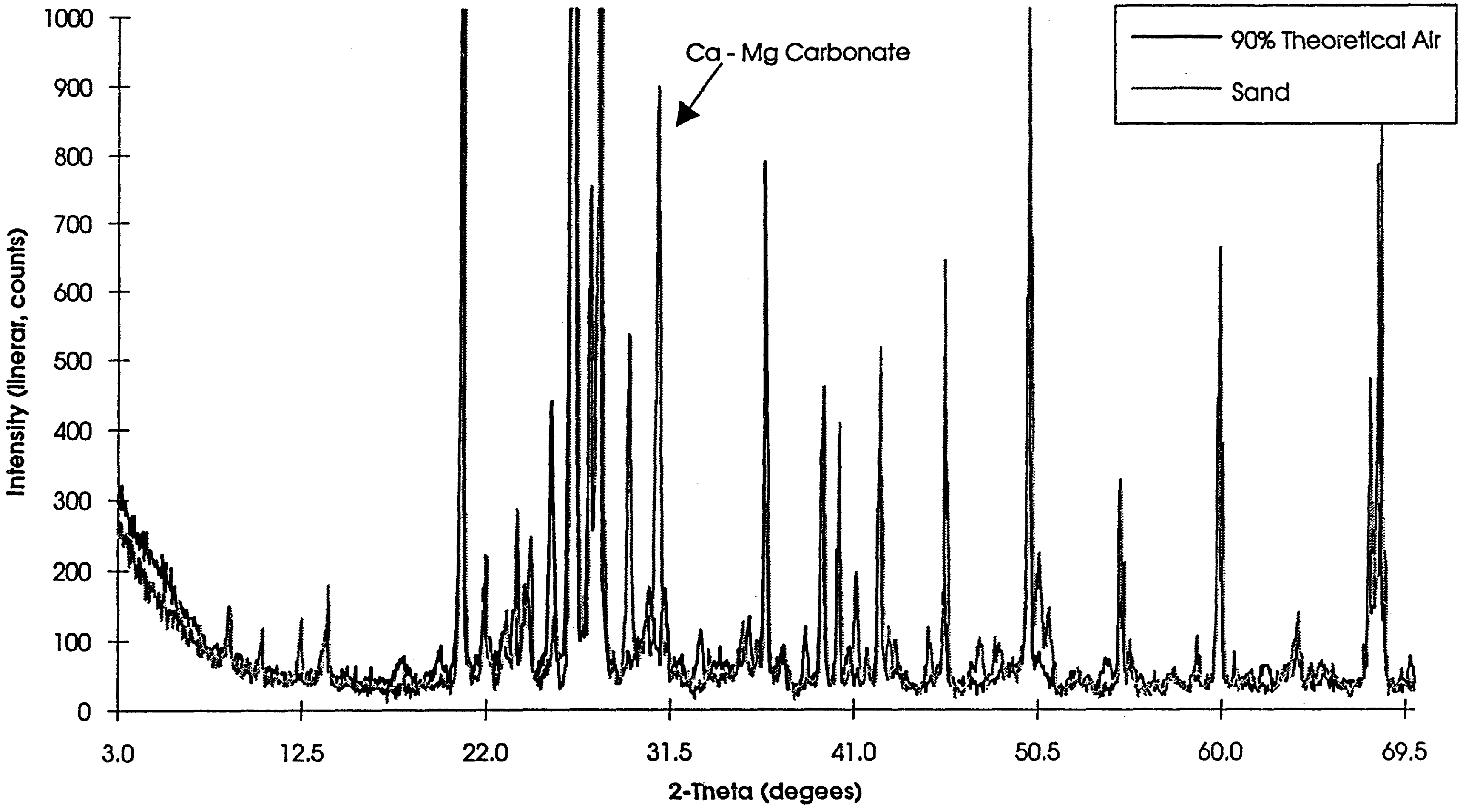

Figure 3. Comparison of x-ray diffraction patterns for bed sand and unagglomerated bed material combusted at 90% theoretical air.

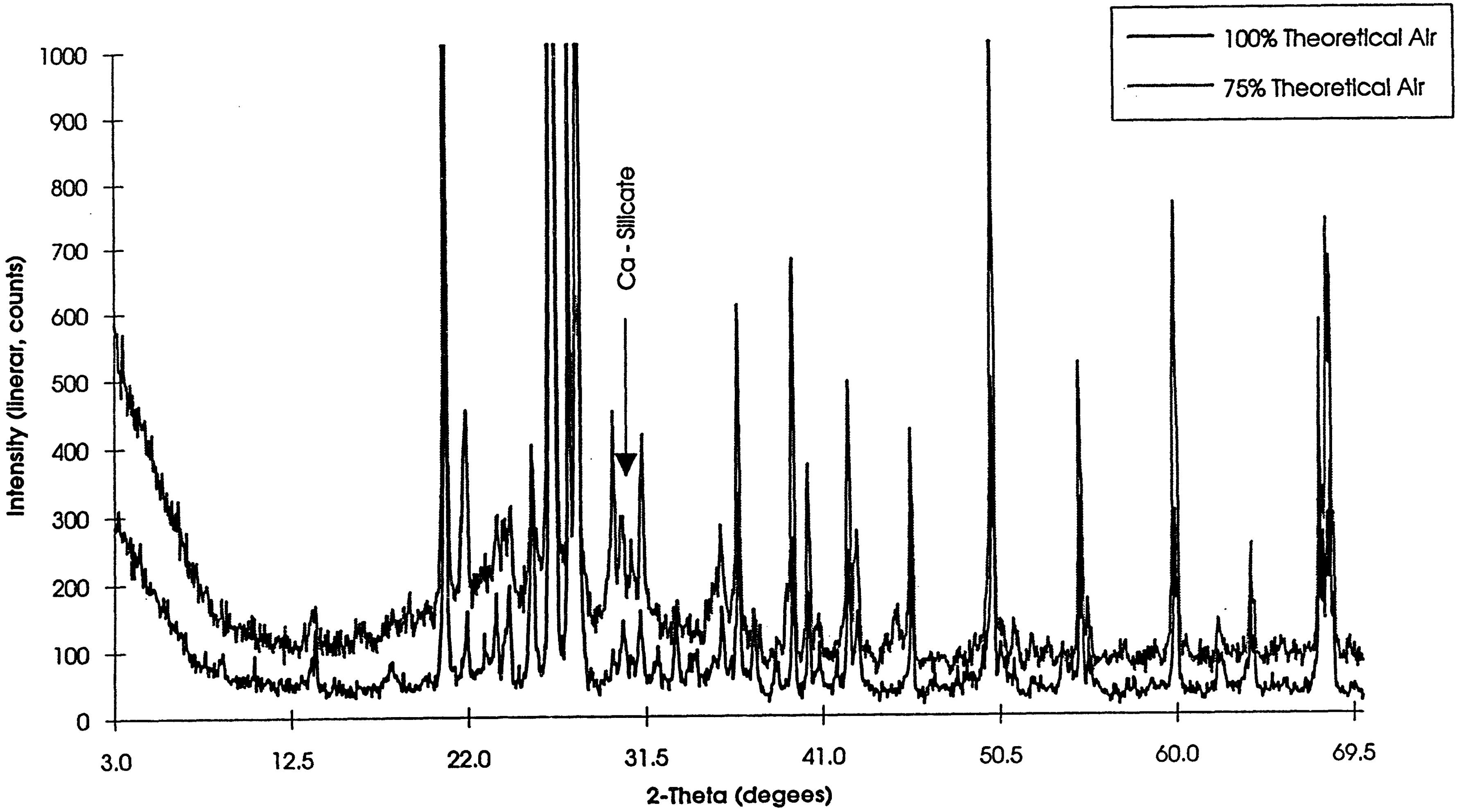

Figure 4. Comparison of x-ray diffraction patterns for unagglomerated bed material combusted at 90% theoretical air and agglomerated bed material combusted at 75% theoretical air

Because of the high alkalies in the glass (Na, K, and Ca; Table 2 analyses 127-132), we suspect this material was derived either from feldspar minerals from the sand bed or from clays within the coal. The glass is also high in iron, magnesium, and calcium. These elements were most likely derived from two sources: the iron from fluxing reactions with iron pyrites in the coal and the calcium and magnesium from dolomites in the sand bed. All three of these elements may have contributed to lowering the melting temperature of the aluminosilicates.

Table 2. Microprobe traverse across quartz grain into glass produced from a melt (Wt%.).

	Analyses	SiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	SO_3	Total
Quartz	119	100.8	0.11	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	100.99
↓	120	99.78	0.25	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.08
	122	99.13	0.19	0.05	0.00	0.00	0.01	0.01	0.00	0.00	0.00	99.38
	123	100.6	0.38	0.05	0.00	0.00	0.05	0.00	0.00	0.03	0.00	101.16
	124	101.1	0.03	0.05	0.00	0.00	0.03	0.00	0.00	0.00	0.01	101.30
	125	95.59	4.09	0.10	0.03	0.00	0.11	0.01	0.01	0.01	0.03	99.98
	126	83.70	5.65	0.11	0.00	0.00	0.22	0.01	0.01	0.00	0.02	89.72
Melt	127	83.36	5.60	1.65	0.00	0.74	3.12	0.45	0.99	0.03	0.06	96.00
↓	128	59.05	7.30	4.42	0.08	5.38	18.85	1.52	3.18	0.09	0.10	99.98
	129	54.60	8.10	4.18	0.02	5.20	20.50	1.53	2.79	0.13	0.12	97.17
	130	54.33	7.95	4.12	0.03	5.77	21.45	1.63	2.66	0.10	0.16	98.21
	131	55.92	7.27	4.58	0.09	5.67	21.06	1.71	2.78	0.13	0.14	99.34
	132	56.11	7.42	4.35	0.05	5.69	20.77	1.65	2.85	0.10	0.20	99.18

The other dominate mineralogical reaction in the agglomerates may be the result of solid-solid reactions involving calcium and magnesium with aliumnosilicate minerals or calcium and magnesium with the aluminosilicate melt. Figure 2 is a photomicrograph showing "blade-like" minerals forming around a quartz grain. Some of the newly-formed minerals in the agglomerate have a crystal form termed "spinifex fabric" by mineralogists. This texture is an array of criss-crossing sheaves of mineral crystals which, in nature, are commonly the minerals olivine or aluminous clinopyroxene. Spinifex textures have also been found in metallurgical slags and in silicate melts that have been undercooled drastically below the range of normal nucleation and crystal growth (Best, 1982).

Table 3. Representative microprobe analyses of mineral products in agglomerated material (Wt%.).

Analyses	SiO_2	Al2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	SO_3	Total
209	46.13	13.68	4.95	0.11	10.69	23.37	0.99	0.39	0.39	0.16	100.85
210	48.29	12.34	4.32	0.10	7.91	22.29	2.49	1.07	0.34	0.51	99.66
211	44.97	12.86	5.21	0.11	11.71	23.79	0.76	0.33	0.34	0.33	100.41

Based on the x-ray diffraction and electron microscopy data, these minerals appear to be single chain silicate minerals, perhaps the pyroxene, diopside. It may be possible that these areas represent the intergrowth of two mineral phases. Even though potassium is relatively low (less than 1 wt%), it is difficult to fit a cation of this size into the pyroxene structure, suggesting the possibility of multiple phases.

Future Work

Work planned for the next quarter includes continuation of theoretical air tests. Analyses of agglomerated and unagglomerated materials will accompany these tests. Also, analyses of deposits from additional industrial fluidized bed combustors will be reported.

References

Best, M.G., *Igneous and Metamorphic Petrography*, Freeman, San Francisco, 1982.

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