DOE/PC/92530--T6

MAR 02 1994

M-1
1

Bed Material Agglomeration During Fluidized Bed Combustion

Technical Progress Report for the Period
October 1, 1993 - December 31, 1993

Robert C. Brown, M. Robert Dawson, and Jerod L. Smeenk

Iowa State University
Ames, IA 50011

Work Performed Under Grant
No. DE-FG22-92PC92530

Date Transmitted: January, 1994

Prepared for: U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA

Project Monitor: Wu Lan

RECEIVED
USDOE/PETC
94 FEB 10 PM 3:18
ACQUISITION & ASSISTANCE DIV.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Bed Material Agglomeration During Fluidized Bed Combustion

Technical Progress Report for the Period
October 1, 1993 - December 31, 1993

Robert C. Brown, M. Robert Dawson, and Jerod L. Smeenk

Iowa State University
Ames, IA 50011

Work Performed Under Grant
No. DE-FG22-92PC92530

Date Transmitted: January, 1994

Prepared for: U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA

Project Monitor: Wu Lan

RECEIVED
USDOE/PETC
94 FEB 10 PM 3:18
ACQUISITION & ASSISTANCE DIV.

MAR 02 1994

M-1
1

RECEIVED
MAY 02 1994
OSTI

Bed Material Agglomeration During Fluidized Bed Combustion
Technical Progress Report
October 1, 1993 - December 31, 1993

Robert C. Brown, M. Robert Dawson, and Jerod L. Smeenk
Iowa State University, Ames IA 50011

Abstract

During this quarter, agglomerates which formed in the FBC at Montana-Dakota Utilities (Heskett Station Unit 2 located in Bismarck, ND) were analyzed by x-ray diffraction analyses (XRD) for mineral determination; bulk chemical composition was determined by inductively coupled plasma spectroscopy; and polished sections were made for optical and scanning electron microscopy. Polarized-light microscopy was performed using a Zeiss research microscope. Individual mineral grains were analyzed using an ARL electron microprobe and a JOEL 840 scanning electron microscope.

The agglomerate was found in the mechanical dust collector and was about ten centimeters in diameter with a dark-colored core and a greenish rim. The sample had voids up to ten millimeters in size; however, the agglomerate was hard to break apart. Bulk compositionally, the agglomerate consists primarily of calcium, silica, and alumina with relatively high abundances of iron (8 to 9 wt%), magnesium (5 to 9 wt%) and sodium (3 to 4 wt%). Mineralogically, the agglomerate consists primarily of tabular minerals which range in length from $< 50 \mu\text{m}$ to 0.5 mm. These minerals are most commonly randomly oriented, with larger crystals growing in void spaces, or they are sometimes radial in habit. Most of the minerals in this deposit are in the melilite group (gehlenite, melilite, and akermanite) and pyroxene group (diopside and augite). Akermanite occurs in nature when sandy limestones or dolomites are heated by geologic processes. These minerals have also been described in "buchites" or partially fused rocks produced by the in situ, near-surface natural combustion of coal seams with interlayered shale and sand. The melilite minerals commonly form from and break down to pyroxene minerals. During these solid-phase reactions, the temperature of formation of the melilite minerals can be lowered by a reduction of the partial pressure of CO_2 (Diopside + Calcite $\rightarrow$ Akermanite).

It is likely that the "root" cause of this agglomerate originated in the dense phase of the FBC bed. Because fluidized bed combustors work below the ash fusion temperature of coal ash, aluminosilicates (clays) in the ash probably became "sticky" due to fluxing reactions with pyrite (FeS_2) and perhaps alkalis (Na). This is indicated by the high amounts of iron, silica, and alumina in the agglomerate. Because of the size of the deposit, the bed particles probably agglomerated in the dust collector. Based on our experimental studies, the agglomerate was probably "strengthened" through mineral reactions with incorporated calcium oxides and calcium carbonates from unreacted sorbent. The single-chain silicate minerals (diopside and augite) formed due to solid-solid reactions between agglomerated aluminosilicate material and sorbent. These reactions have been observed in agglomerates formed in our laboratory combustor during tests using less than 80% theoretical air. The magnesium in the agglomerate most likely came from a dolomitic component (magnesium carbonate) in the sorbent. The melilite minerals probably formed when unreacted sorbent was in contact with diopside minerals in the agglomerate. The reactions which lead to the melilite minerals may have been enhanced by a decrease of CO_2 partial pressure in the dust collector.

Bed Material Agglomeration During Fluidized Bed Combustion

Robert C. Brown, M. Robert Dawson, and Jerod L. Smeenk

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

Analyses of agglomerates formed in Utility-scale FBCs

During this quarter, agglomerates which formed in the FBC at Montana-Dakota Utilities (Heskett Station Unit 2 located in Bismarck, ND) were analyzed by x-ray diffraction analyses (XRD). Bulk chemical composition was determined by inductively coupled plasma spectroscopy. 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

The agglomerate received from the Heskett Station combustor was found in the mechanical dust collector. The agglomerate was about ten centimeters in diameter with a dark colored core and a greenish rim. The sample had voids up to ten millimeters in size; however, the agglomerate was hard to break apart. Table 1 contains the bulk chemical analyses of the deposit core and rim (with the exception of silica and alumina which are still in progress at the time of this report). Table 2 is a list of mineral phases found in the rim and core of the deposit and an estimate of the relative percentage of the mineral phases. Table 3 shows electron microprobe analyses of minerals obtained from thin sections made from the agglomerate. Figures 1 and 2 are optical photomicrographs which show examples of the mineral phases that are present.

Table 1. Major and minor (wt.%) element abundance in the clinker found in the dust collector at the Heskett Station Unit 2, Montana Dakota Utilities. Silica and Alumina total to between 55 and 65 wt% (analyses are in progress at the time of this report).

	Green Rim	Dark Core	STD ^a	Publ ^b
Fe ₂ O ₃	7.91	8.76	14.3	13.44
MgO	5.25	8.61	1.76	1.8
CaO	16.2	24.1	15.4	15.9
Na ₂ O	3.09	3.43	3.04	3.05
K ₂ O	1.71	0.69	2.20	2.26
TiO ₂	0.52	0.60	1.37	1.33
P ₂ O ₅	0.18	0.27	0.39	0.38
S	0.45	0.60	0.13	0.18

a STD = analyses of standards used to monitor accuracy of analyses

b Publ = published values of standards

Table 2. Minerals present in agglomerate from Heskett Station Unit 2, Montana Dakota Utilities Utilities.

<u>Minerals present:</u>	<u>Approximate %</u>
<u>Rim</u>	
Diopside Ca(Mg,Al)(Si,Al) ₂ O ₆	34
Akermanite Ca ₂ MgSi ₂ O ₇	19
Quartz SiO ₂	13
Gehlenite Ca ₂ Al(Al,Si) ₂ O ₇	5
possible: Calcium Strontium Aluminum Silicate CaSrAl ₂ SiO ₇	21
possible: Nepheline (K,Na)AlSiO ₄	6
possible: Sodium Aluminum Silicate Hydrate Na ₁₂ Al ₁₂ Si ₁₂ O ₄₈ · xH ₂ O	2
<u>Core</u>	
Akermanite Ca ₂ MgSi ₂ O ₇	73
Augite Ca(Fe,Mg)Si ₂ O ₆	10
Quartz SiO ₂	5
Possible: Iron Sulfide FeS	12

Table 3. Electron microprobe analyses of mineral phases present in the agglomerate from Haskett Station Unit 2, Montana Dakota Utilities.

<u>Analyses</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>FeO</u>	<u>MnO</u>	<u>MgO</u>	<u>CaO</u>	<u>Na₂O</u>	<u>K₂O</u>	<u>TiO₂</u>	<u>SO₃</u>	<u>Totals</u>
Tabular crystals, photo 32											
158	41.53	8.51	1.87	0.02	9.10	35.96	2.93	0.07	0.05	0.02	100.05
159	40.97	8.51	1.65	0.03	9.20	36.48	2.72	0.08	0.08	0.00	99.73
160	42.26	8.83	1.85	0.10	9.16	35.74	2.88	0.09	0.03	0.00	100.94
Fine-grained halo around void, photo 32											
163	40.91	10.11	1.82	0.05	8.77	36.15	2.84	0.08	0.06	0.00	100.79
164	0.14	66.85	13.34	0.20	22.93	0.09	0.00	0.00	0.75	0.00	104.30
165	32.30	11.98	8.66	0.29	6.96	18.99	3.66	0.64	3.28	0.33	87.09
166	0.22	67.57	10.28	0.13	24.94	0.13	0.00	0.00	0.78	0.00	104.05
167	39.55	11.45	1.36	0.03	8.91	37.10	2.12	0.06	0.02	0.00	100.61
Blocky crystal in matrix, photo 32											
170	40.03	0.13	10.50	0.26	46.96	1.57	0.01	0.00	0.04	0.00	99.49
171	40.69	0.31	8.56	0.27	48.93	2.10	0.05	0.00	0.07	0.00	100.99
Fine-grains around Blocky grain, photo 32											
174	42.36	7.66	2.20	0.03	9.48	36.26	2.64	0.09	0.04	0.00	100.76
175	41.33	9.23	1.67	0.03	8.91	36.77	2.49	0.07	0.06	0.00	100.55
178	47.18	11.19	4.65	0.05	12.43	24.33	0.26	0.00	1.43	0.00	101.52
179	48.75	9.16	4.31	0.08	13.82	24.77	0.25	0.01	0.91	0.00	102.07
180	46.43	10.70	5.33	0.05	12.20	24.23	0.25	0.00	1.31	0.00	100.51
Birefringent grain, photo 25											
183	50.78	7.31	3.54	0.12	14.87	24.45	0.15	0.00	0.90	0.00	102.12
184	43.27	15.05	5.54	0.08	10.90	24.06	0.26	0.00	2.17	0.00	101.32
185	41.47	15.35	5.98	0.09	9.94	23.63	0.40	0.06	2.59	0.00	99.50
Random matrix, photo 25											
188	46.61	25.62	4.76	0.14	0.87	3.29	10.87	4.20	0.33	0.33	97.03
189	46.43	23.29	6.04	0.23	2.04	6.46	8.82	3.19	0.74	0.18	97.39
190	45.63	21.19	8.28	0.21	3.58	10.87	8.18	2.60	0.71	0.26	101.50
Lighter colored matrix, photo 25											
193	47.18	27.91	4.95	0.12	0.23	1.63	12.75	3.82	0.13	0.70	99.41
194	46.62	23.74	6.85	0.17	1.29	5.01	10.04	4.28	0.24	0.74	98.96
195	44.39	15.81	14.63	0.51	2.92	9.58	6.66	2.94	0.48	0.89	98.81

<u>Analyses</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>FeO</u>	<u>MnO</u>	<u>MgO</u>	<u>CaO</u>	<u>Na₂O</u>	<u>K₂O</u>	<u>TiO₂</u>	<u>SO₃</u>	<u>Totals</u>
Blocky crystal, photo 27											
198	43.47	7.01	2.46	0.01	9.75	35.72	2.76	0.11	0.00	0.00	101.29
199	43.78	6.59	1.89	0.06	10.32	36.56	2.42	0.07	0.01	0.00	101.70
200	42.69	7.00	2.04	0.03	9.78	36.32	2.66	0.07	0.00	0.01	100.59
Traverse from blocky grains to long tabular grains, photo 27											
203	46.08	13.69	4.24	0.09	11.92	24.40	0.27	0.00	1.50	0.00	102.19
204	46.52	13.03	4.16	0.07	11.88	24.64	0.23	0.00	1.57	0.01	102.11
205	45.22	12.96	4.08	0.06	12.12	24.64	0.27	0.00	1.84	0.00	101.18
206	45.86	12.90	4.03	0.05	12.06	24.54	0.29	0.01	1.84	0.01	101.59
207	47.78	11.66	3.86	0.10	13.05	24.73	0.26	0.00	1.64	0.03	103.10
208	48.08	10.77	2.98	0.11	13.77	25.16	0.25	0.00	1.39	0.00	102.50
209	45.51	13.21	3.60	0.07	12.03	24.58	0.30	0.00	1.96	0.00	101.26
210	46.97	12.87	3.61	0.05	12.14	24.50	0.22	0.01	1.89	0.00	102.26
211	48.67	10.54	2.96	0.05	13.57	24.83	0.24	0.00	1.41	0.00	102.27
212	46.87	11.48	3.96	0.00	12.66	24.33	0.24	0.00	1.62	0.00	101.16
213	46.61	12.49	4.34	0.10	11.94	24.56	0.31	0.01	1.78	0.00	102.14
214	44.74	13.76	4.54	0.08	11.75	24.37	0.34	0.00	1.91	0.00	101.48
215	44.83	13.88	4.88	0.14	11.57	24.31	0.43	0.00	1.73	0.00	101.77
216	45.15	14.39	5.05	0.07	10.92	24.23	0.33	0.01	1.38	0.04	101.57
217	44.55	15.03	5.61	0.15	10.77	24.53	0.31	0.01	1.06	0.00	102.03
218	44.51	15.69	5.77	0.09	10.65	24.47	0.31	0.00	1.19	0.00	102.68
219	44.97	15.12	5.62	0.09	9.85	24.40	0.26	0.02	1.33	0.01	101.66
220	44.31	15.79	5.12	0.05	7.62	23.10	0.19	0.00	1.18	0.03	97.40
221	44.79	15.03	6.02	0.08	10.97	24.40	0.31	0.01	1.48	0.00	103.08
222	43.51	15.03	5.73	0.09	10.41	24.27	0.36	0.02	1.55	0.01	100.98
223	41.29	20.29	5.85	0.14	9.70	22.56	0.38	0.03	1.40	0.04	101.66
224	44.23	14.74	6.44	0.10	10.27	24.35	0.33	0.03	1.45	0.00	101.94
225	44.05	14.73	6.45	0.12	10.55	24.19	0.36	0.01	1.40	0.00	101.86
226	44.48	14.33	6.33	0.15	10.61	24.23	0.33	0.00	1.29	0.00	101.75
227	44.45	14.69	6.31	0.10	10.33	24.37	0.38	0.02	1.34	0.00	101.98
228	44.37	14.60	5.93	0.12	10.61	24.44	0.38	0.01	1.40	0.00	101.85
229	44.90	14.00	5.80	0.15	10.71	24.18	0.34	0.00	1.31	0.00	101.39
230	42.90	14.56	6.01	0.07	10.58	23.92	0.40	0.00	1.54	0.00	99.97
Fine-grained region											
233	37.77	12.26	0.75	0.00	8.86	37.72	1.61	0.06	0.04	0.00	99.07
234	39.42	10.87	1.92	0.04	9.53	37.66	1.68	0.05	0.03	0.00	101.21

Figure 1. Radial crystal growth in deposit from a dust collector at the Heskett Station Unit 2, Montana Dakota Utilities. Field of view is 0.7 millimeters.

Figure 2. Calcium aluminosilicate minerals growing into voids. These minerals also contain high amounts of iron and magnesium. Field of view is 2.7 millimeters.

The deposit consists primarily of calcium, silica, and alumina. The deposit also contains relatively high abundances of iron (8 to 9 wt%), magnesium (5 to 9 wt%) and sodium (3 to 4 wt%). As can be seen in Figures 1 and 2, the agglomerate consists of mostly tabular minerals. These range in length from less than 50 micrometers up to 0.5 millimeters. These minerals are sometimes in a radial habit (Figure 1) or, more commonly, randomly oriented with larger crystals growing in void spaces (Figure 2).

Most of the minerals which formed in the deposit are in the melilite group (gehlenite, melilite, and akermanite, Table 2) and pyroxene group (diopside and augite). Akermanite and gehlenite melt congruently at 1454°C and 1590°C respectively, and form a solid solution series with a minimum melting temperature at 1385°C (ref. 1). Natural melilites can contain appreciable amounts of iron and sodium which causes a lowering of the melting temperature; however, the melting temperatures of these phases are still well above the operating temperatures of a fluidized bed combustor. In a solid-phase reaction, the temperature of formation of these minerals can also be lowered by a reduction of the partial pressure of CO₂ (Figure 3 from ref 2, reaction 27, Diopside + Calcite → Akermanite). The melilite group of minerals are also unstable below 500°C and break down to form clinopyroxenes (diopside and augite, single chain silicate minerals).

Figure 3. P_{CO2} - T diagram illustrating the effect of CO₂ pressure on reaction 27 (from ref 3).

Akermanite occurs in nature when sandy limestones or dolomites are heated by geologic processes. Melilite is also formed when basic magmas interact with carbonate rocks. These minerals have also been described in "buchites" or partially fused rocks produced by the in situ, near-surface natural combustion of coal seams, particularly coal seams with interlayered shale and sand (ref 3).

It is likely that the causes of this agglomerate originated in the dense phase of the FBC bed. Because fluidized bed combustors work below the ash fusion temperature of coal ash, the ash probably became "sticky" due to fluxing reactions of pyrite (FeS_2) with aluminosilicates (clays) in the coal. This is indicated by the high amounts of iron, silica, and alumina in the agglomerate. The bed particles probably agglomerated in the dust collector. Once in the dust collector, the agglomerate "strengthened" through mineral reactions which incorporated calcium carbonates from unreacted sorbent. The single-chain silicate minerals (diopside and augite) formed due to solid-solid reactions between agglomerated aluminosilicate material and sorbent. These reactions have been observed in agglomerates formed in our laboratory combustor during tests using less than 80% theoretical air. These mineral reactions occurred without melting aluminosilicates from the ash. The magnesium in the agglomerate most likely came from a dolomitic component (magnesium carbonate) in the sorbent. The melilite minerals probably formed when unreacted sorbent was in contact with diopside minerals in the agglomerate. The reactions which lead to the melilite minerals may have been enhanced by a decrease of CO_2 partial pressure in the dust collector.

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

1. Deer, Howie, and Zussman, *An Introduction to the Rock Forming Minerals*, Logman, 1978.
2. Tracy, R. J. and Frost, B.R., Phase Equilibria and Thermobarometry of Calcareous, Ultramafic and Mafic Rocks, and Iron Formations, in *Contact Metamorphism*, D. M. Kerrich, ed., Mineralogical Society of America, Reviews in Mineralogy, V.26, 1991.
3. Foit, F. F., Hooper, R. L., and Rosenberg, P. E., An unusual pyroxene, melilite, and iron oxide mineral assemblage in a coal-fir buchite from Buffalo, Wyoming, *American Mineralogist*, V. 72, 137-147, 1987.

END

DATE
FILMED

5/16/94