BED AGGLOMERATES FORMED BY ATMOSPHERIC FLUIDIZED BED COMBUSTION OF A NORTH DAKOTA LIGNITE

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INTRODUCTION

The goal of atmospheric fluidized bed combustion (AFBC) research at the Grand Forks Energy Technology Center is to provide a data base for design, operation, process control, and emission control requirements for low-rank coals. The application of the AFBC process has the potential to solve some of the problems associated with conventional combustion. These problems are ash fouling on heat exchange surfaces, the expense and reliability of SO_2 control devices such as scrubbers, and the system sensitivity to fuel variables (moisture, Na_2O concentration, etc.).

These problems can be reduced by the AFBC process for low-rank coals because the alkaline characteristics of the ash or sorbent added directly to the combustion zone provides the sulfur retention, which would eliminate or reduce the need for post combustion SO_2 controls. The temperatures in the combustion zone are at the right levels to provide maximum reaction of SO_2 and alkali to form solid alkali sulfate waste. One problem which the fluidized bed combustion of low-rank coals seems to exhibit is a tendency toward the formation of agglomerates of the material which are used to make up the bed. Agglomerates in this case are defined as a cluster of individual bed material particles held together by a substance not yet well understood, and manifest in many differing forms. The understanding of the mechanism of formation of these agglomerates is vital to their control, and therefore the full utilization of low-rank coal in AFBC.

Once formed these agglomerates will tend to decrease heat transfer, and fluidization quality resulting in poor combustion efficiency and loss of control of bed operational parameters (i.e., excess air, temperature, etc.). In severe cases the formation of agglomerates can lead to a forced premature shutdown of the system.

While the addition of limestone, or calcium bearing materials into the fluid bed, or the forming of the bed itself by limestone particles has shown a tendency to inhibit the formation of agglomerates, agglomerates of a severe nature have been observed in a bed of limestone alone, or limestone and sand particle mixtures while burning a high sodium coal for an extended period of time.

In general with a high sodium coal the agglomeration of limestone bed material is dependent only on the length of run time, if the run is long enough agglomeration in a limestone bed will occur, and can be as devastating as those which occur with a silica bed.

GFETC constructed a 0.2 square meter experimental AFBC. A detailed description of the unit is given by Goblirsch and others (1). The combustor can be operated over a wide range of conditions as listed below:

Average bed temperature	--	700 to 982°C
Superficial gas velocity	--	0.9-2.7 m/sec
Excess air	--	10 to 50%
Ash reinjection (% of primary cyclone catch)	--	0 to 100%.

The nominal coal feed rate is 80 kg/hr at 1.8 m/sec superficial gas velocity and 20% excess air.

This paper discusses the performance of quartz or limestone as a bed material during the combusting of high sodium North Dakota lignite. The lignite is from the Beulah mine of Mercer County, North Dakota. The composite coal and coal ash analysis is summarized in Table 1. The lignite was partially dried before this series of tests; its as-mined moisture content was 36%, and its heating valve 15,000 J/g.

TABLE 1. TYPICAL COAL AND COAL ASH ANALYSIS OF HIGH Na BEULAH LIGNITE

Ultimate Analysis, As Fired			Coal Ash Analysis, % of Ash	
Carbon	52.65	%	SiO_2	15.8
Hydrogen	4.59		Al_2O_3	12.1
Nitrogen	0.75		Fe_2O_3	9.9
Sulfur	1.33		TiO_2	0.8
Ash	9.7		P_2O_5	1.0
Moisture	20.0		CaO	17.5
Heating Valve (8372 Btu/lb)	19,459 J/g		MgO	6.2
			Na_2O	8.8
			K_2O	0.0
			SO_3	27.2

Other important considerations are the operation of the combustor and how operational parameters affect the performance of the bed material, sulfur retention on coal ash and bed material, and heat transfer. The most important operational parameters of the AFBC for the tests to be discussed here are listed in Table 2.

TABLE 2. AFBC OPERATIONAL PARAMETERS

Run Number	2181	2281	2481
Coal Type	Beulah	Beulah	Beulah
Bed Material	Quartz	Limestone	Limestone
Average Bed Temperature (°F)	1467	1460	1450
Superficial Gas Velocity (M/sec)	1.8	2.0	1.8
Excess Air (%)	25.49	22.65	24.98
Additive	None	*	*
Ash Reinjection (%)	None	100	100
Coal Feed Rate (kg/hr)	53	57	48

*Addition of supplemental bed material to maintain bed depth.

The tendency for the bed to agglomerate has been shown through extensive testing to depend on the following parameters:

1. Bed temperature (higher temperature increases tendency)
2. Coal sodium content (increased coal sodium content shows increased severity of agglomeration)

3. Bed material composition (high calcium content tends to delay, and decrease the severity of agglomerates formed)
4. Ash recycle (increased recycle of ash tends to increase agglomeration tendency)
5. There appears to be a bed design parameter such as position of coal feed points, and distributor plate performance which affect bed material agglomeration.

The bed material used in baseline run 2181 was 10 mesh quartz sand. Upon startup the bed was sampled every eight hours for the duration of the 69 hour run. At the end of the run the system was cooled and opened to expose the inside of the combustor. The bed material was removed and several agglomerates were found, which varied in size and shape, with the largest having a diameter of 6 cm. These agglomerates were found both free floating in the bed and attached to the inside wall of the combustor.

The limestone bed material was tested in run 2281 using 100% ash reinjection for a duration of 73 hours. The bed was sampled in the same manner as 2181. The formation of agglomerates in the run was very minimal with no major agglomerates found. On the other hand, run 2481 which used a limestone bed ran for 160 hours with 100% ash reinjection and had severe problems with agglomeration. After the run numerous agglomerates were found loose in the bed. In addition, a large agglomerate was found on top of the distributor plate at the bottom of the combustor. The agglomerate had dimensions of 30.5 cm X 30.5 cm X 12.5 cm; it weighed 10 kg and covered 30% of the distributor plate.

The bed material and agglomerates were characterized by polished thin section study, polarized light microscopy, and scanning electron microscopy/microprobe (SEM) - both secondary electron (SEI) and backscatter electron (BEI) images were used. Bulk samples were analyzed by x-ray diffraction and x-ray fluorescence. The goals in characterizing the bed material and agglomerates are to identify the stages which lead to agglomeration and possibly postulate a mechanism of their formation to thereby determine methods and procedures to control their growth.

RESULTS AND DISCUSSION

Quartz Bed Agglomerates

Agglomeration of quartz bed material is typified by run 2181 utilizing high-Na Beulah lignite and ash injection. Samples of bed material taken at various intervals during the run are illustrated in Figures 1 to 11 with chemical analyses data given in Table 3. The following four stages can be used to summarize the agglomeration process:

Stage 1. Initial ash coating.

Initial samples of bed material have a fine coating, about 50 microns thick, consisting of sulfated aluminosilicate particles (Figure 1). The coatings contain some coarser ash materials in the outer parts and the inner parts have penetrated the quartz grains slightly along gently curved or cuspate embayments. The quartz grains are extensively fractured, apparently as a result of thermal stresses.

Stage 2. Thickened nodular coatings.

Longer bed usage results in the development of thicker ash coatings about 100 - 300 microns thick with nodular outer surfaces resulting from incorporation of larger ash particles (Figure 2). Sulfating, shown by lighter colored areas in the SEM photographs, is common within both the finer and coarser ash particles of the coating.

Stage 3. Sulfated ash-cemented agglomerates.

In this stage the quartz grains are loosely held together by a cement of sulfated aluminosilicate ash (Figure 3). Penetration of quartz grains by fine grained ash is more extensive.

Stage 4. Glass-cemented agglomerates.

In the final stage quartz grains are bonded by sulfated ash which has partly melted and crystallized through reaction of the hot ash and the quartz grains. Resultant cooled agglomerates consist of quartz grains of the bed material bonded by a mixture of sulfated ash and Ca-rich, S-poor glass (Figure 4), with an intermediate reaction zone made up of an S-depleted, Si-enriched ash portion with a fringe of melilite or augite crystals projecting into the glass (Figures 5 and 6). Some quartz grains are partly melted and/or recrystallized to cristobalite or other phases.

Limestone Bed Agglomerates

Agglomeration of limestone bed material appears to be dependent on ash deposition and sulfation combined with extensive reaction and deterioration of the bed material.

Ash buildup on the grains and sulfating is comparable to reactions that occur with the quartz bed material. However, the limestone grains appear to undergo the following reactions:

1. Loss of CO_2 and conversion to CaO with addition of S, Fe, Na and other elements. These reactions produce concentric alteration zones, high Ca and S contents and the reddish color that characterizes typical grains (Figure 7).

2. Continued reaction produces thicker sulfated ash coatings and more thoroughly altered bed grains.

3. Bed grains disintegrate extensively and become mixed with ash coatings producing a weakly bonded agglomerate consisting of masses of sulfated ash and altered limestone bed grains and fragments (Figure 8). The altered limestone appears to recrystallize to coarse crystals of anhydrite in a fine-grained matrix containing abundant Ca, S and Si (Figure 9). Other phases, not yet identified, occur in the limestone agglomerates including crystalline Fe-Ca oxides as shown in Figure 10, and other iron-rich zones and coatings.

Where quartz and limestone bed materials are combined mutual interactions produce reaction zones on the quartz containing secondary needles of an unknown calcium silicate mineral (Figure 11).

Bulk x-ray diffraction analyses were performed on the bed material agglomerates to identify the phases present. The crystaline phases found in the quartz bed agglomerates from run 2181 include quartz, a member of the series $Ca_2Al_2SiO_7$-$Ca_2Mg_2SiO_7$ which includes melilite, and $CaSO_4$. The major phases identified in the limestone bed agglomerate are $CaSO_4$, $CaSiO_4$ and CaO. This data supports the SEM microprobe data.

X-ray fluorescence analysis was performed on bed material sampled continually throughout the run to determine the changes in composition of major ash constituents. The most appreciable changes which occurred in the quartz bed run were: SiO_2 decreased from 95 to 47% of the bed because of dilution; SO_3 increased to 24% because of adsorption by alkali constituents of the coal ash in the bed; CaO increased to 11% and Na_2O increased to 7% of the bed. The CaO and Na_2O reacted with the SO_3 and adhered to the quartz grains of the bed. Al_2O_3, Fe_2O_3 and MgO remained relatively constant throughout the run after the initial eight hours. The

components of the limestone bed of run 2481 changed as follows: CaO decreased by dilution to 37% by the coal ash; SO_3 increased to 28% by adsorption; and Na_2O increased to 7.7% of the bed. SiO_2, Al_2O_3, Fe_2O_3 and MgO remained constant throughout the run after the initial eight hours.

The concentrations of alumina and silica remain constant during the run indicating that the aluminosilicate clay particles leave the bed during combustion. On the other hand, the calcium oxide and sodium oxide which largely originate from the organic structure of the lignite are free to react with the SO_2 and bed material increasing their concentration.

TABLE 3. CHEMICAL ANALYSIS DATA FOR FIGURE 1 TO 11.
WT. %

OXIDE	A	B	C	D	E	F	G
SiO_2	10.76	12.45	8.22	12.16	31.20	47.80	48.32
Al_2O_3	11.70	11.20	18.94	8.94	19.13	10.03	10.61
FeO	4.82	0.55	6.94	3.02	13.14	9.95	9.48
MgO	5.71	1.14	11.86	5.73	10.27	4.44	6.26
CaO	18.11	32.86	12.63	12.83	19.82	20.28	20.29
Na_2O	12.70	3.99	10.14	17.97	2.04	6.11	3.73
SO_3	34.45	37.25	30.80	38.27	3.39	0.43	0.52

OXIDE	H	I	J	K	L	M
SiO_2	15.50	19.66	12.39	1.81	0.89	31.50
Al_2O_3	10.28	0.15	5.13	5.91	1.87	8.20
FeO	0.75	0.37	1.15	0.32	81.69	0.56
MgO	3.84	0.09	0.93	0.17	0.91	0.00
CaO	40.45	53.36	44.23	39.58	13.55	44.19
Na_2O	1.91	1.74	0.78	0.40	0.00	2.76
SO_3	21.49	24.39	35.37	51.66	6.33	11.89

CONCLUSIONS

Agglomeration of the bed material can be manifested in many different ways depending on the chemical composition of the bed. The elements which have a major effect are sodium, calcium and sulfur which react with the bed material possibly forming possibly a molten phase. This phase causes other ash constituents to adhere to the bed particles. As this phenomenon reoccurs many times, agglomeration becomes more severe.

REFERENCE

1. Goblirsch, G.M., Vander Molen, R.H., and Hajicek, D.R., AFBC Testing of North Dakota Lignite, Sixth International Fluidized Bed Conference, Atlanta, Georgia, April, 1980.

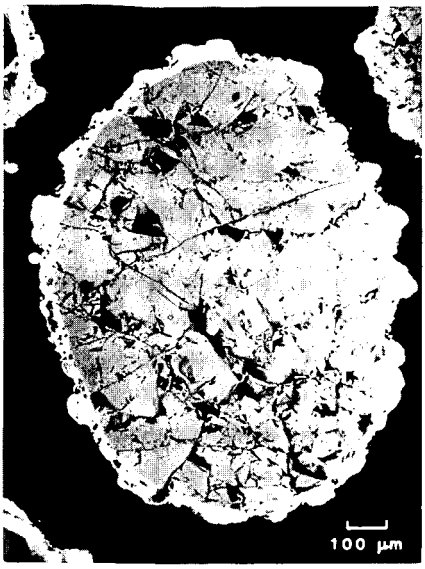

FIG. 1. Initial ash coating on quartz bed material. SEM/BEI image. Analysis A (Table 3). Run 2181, 40 hrs.

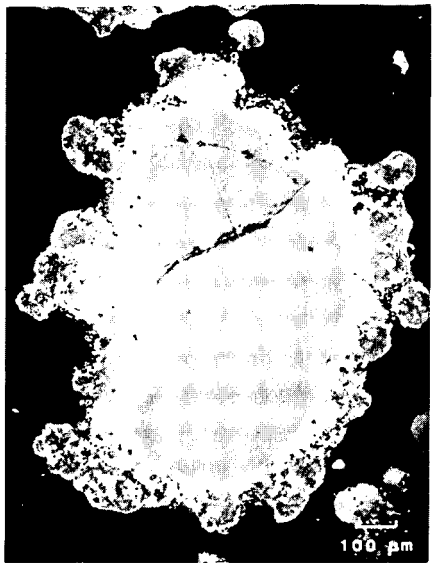

FIG. 2. Thickened nodular ash coating on quartz bed material. SEM/BEI image. Analysis B of fine light sulfated ash and C of darker interior of coarser ash particle (Table 3). Run 2181, 54 hrs.

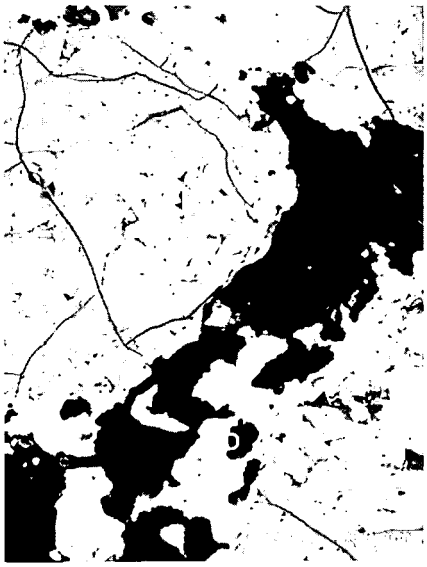

FIG. 3. Quartz bed grains loosely cemented by sulfated aluminosilicate ash. SEM/BEI image. Analysis D given in Table 3. Run 2181, 69 hrs.

FIG. 4. Quartz bed agglomerate bonded by altered sulfated ash, bottom of the dotted boundary (analysis E); Ca-rich, S-poor glass, top of the dashed line (analysis F); and intermediate fringe of melilite or augite crystals. SEM/BEI image. Run 2181, 69 hrs.

FIG. 5. Transmitted light image (partially crossed polars) of lower center of Figure 4 showing light quartz grain, gray glass, and crystals of melilite or augite crystals projecting into glass. Run 2181, 69 hrs.

FIG. 6. Detail of lower center of Figure 5, showing dendritic crystal form of melilite or augite. Analysis G given in Table 3. SEM/SEI image. Run 2181, 69 hrs.

FIG. 7. Concentric alteration zones and reacted limestone bed material. Analysis H given in Table 3. SEM/BEI image. Run 2481, 169 hrs.

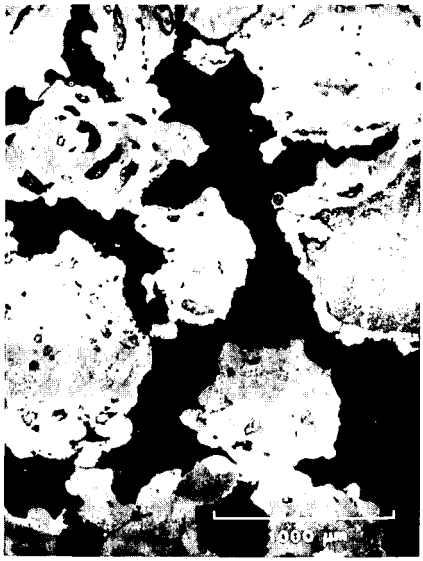

FIG. 8. Weakly bonded agglomerate of sulfated ash and altered limestone bed grains and fragments. Analysis I and J are given in Table 3. SEM/BEI image. Run 2481, 169 hrs.

FIG 9. Limestone bed material altered to coarse crystals of $CaSO_4$ in a fine-grained matrix of Ca, S, and Si. Light area to left is ash coating. Analysis K given in Table 3. SEM/BEI image. Run 2481, 169 hrs.

FIG. 10. Bladed crystals of Fe-Ca oxides in limestone agglomerate. Ash coating to right. Analysis L given in Table 3. SEM/BEI image. Run 2481, 169 hrs.

FIG. 11. Reaction zone consisting of secondary needles of an unknown Ca-silicate mineral on a quartz grain contained in the limestone bed. Analysis M given in Table 3. SEM/BEI image. Run 2481, 169 hrs.